

NUCLEAR SPIN RELAXATION AND MOLECULAR MOTION IN LIQUIDS

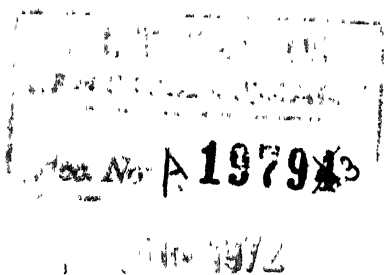
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ANUP KITCHLEW

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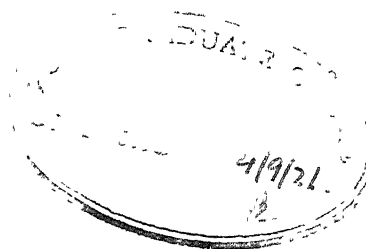
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We dance round in a ring and suppose
But the secret sits in the middle and knows

- Robert Frost

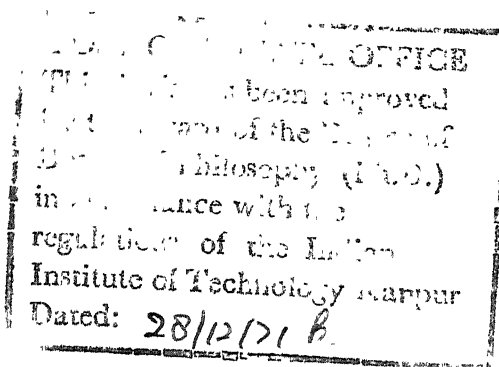


Certified that the work described in this thesis is the original work of Miss Anup Kitchlew performed under my supervision, and has not been submitted elsewhere for a degree.

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SYNOPSIS

SYNOPSIS

This thesis presents a study of the systematics of molecular motion in liquid systems using nuclear spin relaxation technique. Measurements of proton spin-lattice relaxation times, T_1 , and coefficients of self-diffusion, D , have been made as functions of temperature for several liquids from room temperature upto about 40°K below the critical temperature or the temperature at which they might decompose. A spin-echo spectrometer operating at 9.78 MHz was fabricated for this purpose. The liquids studied are thiophene, furan, 2- and 3-bromothiophenes and 1,2-dichloroethane. The experimental results have been analysed in terms of three dominant mechanisms of relaxation, namely, the inter- and intra-molecular dipolar interactions and spin-rotation interactions. The intermolecular contribution has been separated by using the D values measured and the correlation times for molecular reorientation have been determined as functions of temperature. In certain cases where spin-rotation interaction plays a significant role it has been possible to determine the angular velocity correlation times, their temperature dependence and estimate the spin-rotation interaction constant for the molecules.

The first chapter of the thesis introduces the concept of nuclear spin relaxation with special emphasis on those features of relaxation processes in liquids which make this type of study a probe of certain characteristics of molecular motion. This is

followed by a review of the previous work done in this direction and later a discussion of the scope, method and motivation of the present work.

The theoretical framework used in the analysis of the experimental results of this work is described in Chapter II. The equations of motion of magnetization are developed on the basis of the density matrix theory to obtain rigorous expressions for T_1 in terms of the correlation functions for molecular motion. The theoretical features of various important mechanisms of relaxation in liquids have been given. It turns out that only inter- and intramolecular dipolar interactions and spin-rotation interactions are of interest for the present analysis. A brief discussion of Torrey's theory of translational diffusion and Huntress' theory on anisotropic rotational diffusion used in the analysis are given. The existence of multiple exponentials in relaxation decays in molecules containing several spins located at physically inequivalent sites has also been discussed.

Chapter III deals with the description of the spin-echo apparatus fabricated for this work. The essential features of this apparatus are a pulse programmer comprising of Tektronix waveform and pulse generators and some simple circuits. This is used to program the pulses in a desired sequence. These d.c. pulses are used to gate a continuous-wave crystal-controlled oscillator operating at 9.78 MHz. At the output of the gated oscillator radio-frequency (r.f.) voltage of about 300 volts peak

to peak is obtained. The r.f. receiver is a five-stage amplifier-detector assembly tunable from 8-20 MHz and has a net gain of about 10,000 and a bandwidth of 1 MHz. It has a signal to noise ratio of 2:1 for 80% modulation at $3\mu\text{v}$ carrier voltage and takes a maximum input signal of $300\mu\text{v}$. Another important feature of the apparatus is a variable temperature cryostat designed to measure relaxation times from liquid nitrogen temperatures upto about 600°K . All the experiments in this work are performed along the liquid-vapor equilibrium curve by appropriately filling the sample tubes. The samples are prepared free of dissolved oxygen by using freeze-pump-thaw technique and gettering.

Chapter IV describes a study on thiophene and furan in the temperature range 300°K to 550°K and 295°K to 405°K respectively. T_1 varies from 24.0 sec at 300°K to 72.0 sec at 550°K with a maximum of 94.0 sec at 490°K for thiophene. The coefficient of self-diffusion varies from $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ to $38.0 \times 10^{-5} \text{ cm}^2/\text{sec}$ in the same temperature range. In the case of furan T_1 varies from 39.0 sec at 295°K to 66.0 sec at 405°K with a maximum of 95.0 sec at 373°K and D varies from $5.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ to $36.0 \times 10^{-5} \text{ cm}^2/\text{sec}$. The contribution of the intermolecular dipolar interaction has been separated using Torrey's theory. Analysis of the intramolecular interactions gives the temperature dependence of D_\perp , the rotational diffusion constant perpendicular to the plane of the molecule and τ_J , the angular velocity correlation time. D_\perp varies from $0.21 \times 10^{11} \text{ sec}^{-1}$ at 300°K to

$3.5 \times 10^{11} \text{ sec}^{-1}$ at 550°K in thiophene and from $0.37 \times 10^{11} \text{ sec}^{-1}$ at 295°K to $4.02 \times 10^{11} \text{ sec}^{-1}$ at 405°K in furan. τ_J varies from $1.4 \times 10^{-14} \text{ sec}$ at 300°K to $10.8 \times 10^{-14} \text{ sec}$ at 550°K in thiophene and from $1.6 \times 10^{-14} \text{ sec}$ at 295°K to $12.7 \times 10^{-14} \text{ sec}$ at 405°K in furan. Spin-rotation interaction constants for thiophene and furan have been estimated to be about 1.0 kHz and 1.4 kHz respectively. The reorientation is found to be diffusional in character upto 480°K in thiophene and 380°K in furan. The variation of D_\perp with temperature in thiophene obeys an Arrhenius type of equation upto 500°K with an activation energy of 3.2 k cal/mole. However, it does not show such a behaviour in furan.

Chapter V presents T_1 and D measurements on 2- and 3-bromothiophenes in the temperature range 300°K to 450°K and their analysis. Higher temperatures were avoided due to incipient decomposition of the samples. The results show indication of only dipolar interactions contributing to relaxation. The analysis of these results, though somewhat crude due to lack of data on the structural and motional constants, reveals an interesting contrast in the temperature dependences of the rotational correlation times τ_r for these molecules. τ_r varies from $0.23 \times 10^{-11} \text{ sec}$ at 333°K to $0.11 \times 10^{-11} \text{ sec}$ at 450°K with an activation energy of 2.0 k cal/mole in 2-bromothiophene while in 3-bromothiophene it remains essentially constant at about $0.7 \times 10^{-11} \text{ sec}$ over the entire temperature range indicating a large activation energy.

Chapter VI deals with a similar study on 1,2-dichloroethane in the temperature range 300°K to 430°K . The possibility of scalar coupling of protons with chlorine nuclei and intramolecular dipolar interactions modulated by rotamer exchange contributing to relaxation has been examined and found to be negligible. The rotational correlation time is found to vary rather slowly with temperature. This variation is similar to the $T^{\frac{1}{2}}$ dependence predicted by Steele for a spherical top undergoing reorientation dominated by inertial effects. Confirmation of this interpretation, however, needs further experimental and theoretical work on similar molecules.

The significant results of this work are summarized in Chapter VII.

The thesis has three appendices: (i) a note on the reciprocal temperature dependences of the coefficient of self-diffusion, D , and coefficient of viscosity, η , in several organic liquids, (ii) a collection of some of the simple circuits used in the apparatus which are not included in Chapter III and (iii) a description of the Carr-Purcell method for T_2 measurement and its adaptation to the spectrometer.

Chapter I

INTRODUCTION

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INTRODUCTION

I.A Nuclear Spin Relaxation in Liquid Systems

Consider an assembly of nuclear spins each of angular momentum $I \hbar$. In the absence of any external magnetic field the energy levels are $(2I+1)$ -fold degenerate and they are, therefore, equally populated. Now, if a static magnetic field $H_0 \hat{k}$ is applied this degeneracy is lifted to give a set of $(2I+1)$ equidistant levels with energies $(-\gamma m \hbar H_0)$ where $m = -I, -I+1, \dots, +I$. When the field is switched on the system is in a non-equilibrium condition in which these levels are equally populated. The spins eventually attain thermal equilibrium represented by a Boltzmann distribution of populations (at the temperature of the surroundings) among the energy levels by dissipating the excess energy to the other degrees of freedom. The process by which this equilibrium is attained is known as relaxation. This is the same process by which a magnetization $M_0 = \chi_0 H_0$ (χ_0 is the static susceptibility) is obtained along the direction of the field and any magnetization in the perpendicular plane is made to vanish. The motion of the magnetization \vec{M} is represented by a phenomenological equation, given by Bloch¹,

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} - \hat{i} \frac{M_x}{T_2} - \hat{j} \frac{M_y}{T_2} - \hat{k} \frac{M_z - M_0}{T_1}, \quad (\text{I.1})$$

where M_x , M_y and M_z represent the instantaneous magnetizations along the x, y and z axis respectively. The first term refers to

the precession of the magnetization vector about the z-axis with the Larmor frequency

$$\omega_0 = \gamma H_0 \quad . \quad (I.2)$$

T_1 governs the growth of magnetization along the z-axis and is called the spin-lattice (or longitudinal) relaxation time and T_2 the decay of magnetization in the xy-plane and is referred to as the spin-spin (or transverse) relaxation time. These two times can, in general, be different since the growth of populations of the spin states (given by T_1) can proceed at a rate different from that at which the phase coherence between these states is destroyed (given by T_2)².

In a nuclear magnetic resonance (nmr) experiment a radio-frequency (r.f.) magnetic field at the Larmor frequency induces transitions between the energy levels causing a net absorption of energy by the spin system^{3,4}. The strength of the r.f. field that can be used in order that a sustained absorption signal is obtained is governed by the efficiency of relaxation.

Relaxation processes arise due to interactions within the spin system (spin-spin interactions) or due to interactions of the spins with other degrees of freedom termed as 'lattice' (spin-lattice interactions). These interactions manifest themselves in different ways depending upon the physical state of the sample. In diamagnetic solids at low temperatures, for example, the dipole-dipole interactions between nuclear spins produce local fields of the order of several gauss resulting in

broad resonance lines and allows the spin system to attain internal thermal equilibrium much quicker than with the lattice i.e. the T_2 's are much shorter than T_1 's. In a description of relaxation in solids it is necessary to consider all the nuclear spins as forming the spin system because of the tight coupling between them^{4,5}.

In the case of liquids (and gases), however, the situation is quite different. Due to the rapid molecular motion the local fields are usually averaged out leading to narrow resonance lines (having linewidths of the order of fraction of a milligauss) for spin- $\frac{1}{2}$ nuclei in liquids⁶. This also results in T_2 's of the same order of magnitude and often equal to T_1 's in these systems. In the description of relaxation in liquids it is sufficient to consider a group of spins on the molecule (sometimes even the individual spins) as the spin system⁷. The molecular motion plays a crucial role in determining the efficiency of spin relaxation in liquids and, therefore, the study of relaxation under chosen physical conditions could be a significant means for the study of some aspects of molecular motion⁸⁻¹¹. In the next section this point is discussed in some detail.

It may often happen that the relaxation of the spin system does not follow the simple pattern set forth by Eq. (I.1). For solids Eq. (I.1) is found to be certainly inadequate¹². In the case of liquids, however, the form of Bloch equations is found to obtain under a number of generally realizable conditions

although there are exceptions. A rigorous description of the relaxation effects may be obtained by using the density matrix method and this theory indicates clearly the cases where deviations may be expected from Eq. (I.1)^{7,13}. The features of this theory, in so far as they are pertinent for the analysis of the present work, are summarized in Sec. II.A.

I.B Spin Relaxation as a Probe for Molecular Motion

The understanding of nuclear spin relaxation in liquids is chiefly due to the classic theory of Bloembergen, Purcell and Pound (BPP)¹⁴. It was mentioned earlier that in a liquid the local fields at the site of any nucleus, arising from other nuclei in the sample, are averaged out because of the rapid molecular motion. In this theory it was shown that the efficiency of spin relaxation is given by the spectral density, at the nuclear Larmor frequency, of the time correlation functions of such rapidly fluctuating fields. Any spin-lattice interaction may be written as^{7,15,16}

$$H'(t) = \sum_Q (-1)^Q F^Q(t) A^{-Q}, \quad (I.3)$$

where $F^Q(t)$ are the lattice variables which are random functions of time and A^Q are spin operators. The relaxation rate due to this interaction is determined by^{7,14}

$$\frac{1}{T_1} \propto J(\omega) = \int_0^\infty e^{-i\omega\tau} G(\tau) d\tau, \quad (I.4)$$

where

$$G(\tau) = \sum_Q G_Q(\tau) = \sum_Q \langle F^{Q*}(t) F^Q(t+\tau) \rangle_{av} = \sum_Q \langle F^{Q*}(0) F^Q(\tau) \rangle_{av}, \quad (I.5)$$

with $\langle \rangle_{av}$ representing an ensemble average. $F^Q(t)$ are considered stationary random functions of time, $G(\tau)$ is the time correlation function and $J(\omega)$ is its spectral density at the angular frequency ω . If $F^Q(t)$ is given by a Markoff process the correlation function decays exponentially:

$$\langle F^{Q*}(0)F^Q(\tau) \rangle_{av} = \langle |F^Q(0)|^2 \rangle_{av} e^{-|\tau|/\tau_c}, \quad (I.6)$$

where τ_c is the correlation time for the appropriate molecular motion. Substituting Eq. (I.6) in Eq. (I.4) gives

$$\frac{1}{T_1} \propto \sum_Q \langle |F^Q(0)|^2 \rangle_{av} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (I.7)$$

It may seem from Eq. (I.4) that a determination of the relaxation rate, arising from an interaction of known strength, as a function of ω would allow, by Fourier inversion, the determination of $G(\tau)$ as a function of τ for the appropriate lattice function. However, this is not normally feasible since the Larmor frequencies used in nmr experiments range between 1 to 100 MHz while the motional correlation times are in the range of 10^{-11} to 10^{-14} sec so that $\omega \tau_c \ll 1$. This results in the spectral density being independent of frequency, a condition known as 'extreme narrowing'⁷. The relaxation rates, therefore, provide information on the correlation time τ_c given by the integral of the normalized correlation function

$$\tau_c = \frac{\int_0^\infty \langle F^{Q*}(0)F^Q(\tau) \rangle_{av} d\tau}{\langle |F^Q(0)|^2 \rangle_{av}} \quad (I.8)$$

It can be seen that the relaxation times are not sensitive to the actual "shape" of the correlation function but depend on the

areas enclosed by these functions. Such integrals of correlation functions can also be related, quite generally, to appropriate macroscopic transport coefficients¹⁷⁻²⁰.

We shall now consider the various types of correlation times that arise in the description of relaxation processes in liquids. It will be seen that for proton spin relaxation in the diamagnetic liquids studied in this work the only likely mechanisms which contribute significantly to relaxation are the inter- and intramolecular dipolar interactions and the spin-rotation interactions. Why these are the only ones shall be discussed in some detail in Sec. II.B. The intermolecular dipolar interaction is primarily modulated by the relative translational motion of the molecules which involves a translational correlation time τ_t . The intramolecular dipolar interaction is, on the other hand, modulated by the reorientational motion of the molecules involving a rotational correlation time τ_r . The spin-rotation interaction, which is a magnetic interaction of the nuclear spin with the rotational angular momentum of the molecule^{21,22}, is modulated by changes in the angular velocity of the molecule as it reorients²³⁻²⁶. The corresponding correlation time is the angular velocity correlation time τ_J . In certain favourable circumstances it is possible to separate the contribution coming from the different mechanisms, whence the correlation times of molecular motion τ_t , τ_r and τ_J can be estimated. The theoretical calculation of the correlation functions for these interactions is discussed in Sec. II.C and it is shown that if the translational

and reorientational motions are diffusional in character τ_t is related to the coefficient of molecular self-diffusion and τ_r and τ_J to the elements of the rotational diffusion tensor.

The next section summarizes some of the previous theoretical and experimental work aimed at extracting such information on molecular motion in liquids through spin relaxation and in Sec. I.D the scope of the present work is discussed.

I.C Previous Work on Molecular Motion by Spin Relaxation

With the BPP theory¹⁴ providing the basic formulation of the relaxation rates in terms of correlation functions and the density matrix theory of Wangness and Bloch¹³ the rigorous form of the differential equations for macroscopic magnetization, the theoretical problem of spin relaxation in liquids becomes that of calculation of the appropriate correlation functions (or correlation times) on the basis of specific descriptions of molecular motion in liquids.

In the original BPP theory the correlation time τ_t for intermolecular dipolar interaction modulated by translational diffusion is written in terms of the coefficient of self-diffusion D and a hard-sphere radius 'a' for the molecule ($\tau_t = a^2/12D$), and D was related to the coefficient of viscosity η through the Stokes-Einstein relation ($D = kT/6\pi\eta a$, k is Boltzmann constant and T is the temperature in $^{\circ}\text{K}$). Torrey²⁷ has considered this problem in a somewhat rigorous fashion on the basis of the theory of random flights which, in the limiting case

of small mean squared flight paths and small times between flights, goes over to the results given by the equation for isotropic translational diffusion. The derivation of the correlation time in terms of the diffusion equation is briefly discussed in Sec. II.C. For the case of spherical molecules, each containing a spin located at its center, this correlation time is the same as that given by BPP. Hubbard²⁸ considered the case of molecules in which the nuclei are not at the center and showed that this leads to a small correction to the above result. Torrey's formula leads to fairly correct estimates of relaxation rates arising from intermolecular interactions.

For the reorientational motion BPP have used the Debye model of isotropic rotational diffusion originally used in the theory of dielectric relaxation in polar liquids²⁹. This model assumes that the medium surrounding the molecule is continuous so that the rotational diffusion constant D_r is given by the Stoke's formula $kT/8\pi\eta a$. There is considerable evidence that the contribution to relaxation rates calculated by using this formula is much larger than that observed experimentally^{30,31}. The major shortcomings of Debye model are (1) the rotational diffusion may, in general, be anisotropic (2) there may be significant contribution of inertial effects to reorientational processes (3) the use of Stokes-Einstein relation between D_r and η may be questionable for most liquids except possibly for large molecules in solution.

The problem of anisotropic rotational diffusion has been treated by Favro³², Huntress¹⁵, Ivanov³³ and others³⁴⁻³⁶. In the analysis of the results of the present work Huntress¹⁵ theory has been used and shall be discussed in some detail in Sec.II.C. This theory was earlier used to considerable advantage in the analysis of quadrupolar relaxation data to determine the principle values of the rotational diffusion tensor in several liquids³⁷⁻⁴⁰. Steele⁴¹ has evaluated correlation functions where inertial effects are predominant in molecular reorientation starting from the rotational analogue of Langevin equation. Some aspects of this are given in Chapter VI. The approximation of the medium as a continuum, implicit in Stokes formula, is discarded in the above.

The spin-rotation interaction as a mechanism for relaxation in liquids has been discovered recently^{23,24}. In gases, however, this mechanism has been known to contribute significantly to relaxation⁴². Here the molecular collisions that change the orientation also change angular velocity (or rotational angular momentum) and therefore τ_r and τ_J are the same (in the strong collision limit). In the case of liquids, on the other hand, the two correlation times are quite different since angular velocity occurs only during a molecular collision and the correlation functions are different from those for orientation changes²⁴. The existence of this interaction for fluorine relaxation has been observed^{23,26} and recently it has also been seen to contribute to proton relaxation at high temperatures by

Powles and coworkers^{26,43,44}. It is important to note that the temperature dependence of the relaxation from spin-rotation interaction is opposite to that from dipolar interaction and hence the two could be separated if the temperature dependence of relaxation is determined. Another advantage of such a study is that it enables the determination of spin-rotation interaction constants of small magnitudes (~ 1 kHz) which is not usually possible by other methods like molecular beams⁴⁵ and microwave spectroscopy²¹. The correlation times for this interaction can be obtained by using the theory of anisotropic rotational diffusion given by Huntress¹⁵.

There is at present, no general theory available for reorientational motion of molecules which can be applied to all situations. While the limiting conditions of diffusional motion assuming small angular steps in the rotational random walk and that of inertial motion implying essentially free rotation can be handled the intermediate situations are intractable. Furthermore, in any description of reorientational motion the molecular shape plays an important role and it is difficult to simplify the theory to a usable form for all molecular structures. Considerable experimental evidence exists from neutron scattering measurements for the need of a general theory⁴⁶, and the results of nuclear spin relaxation, though somewhat limited in scope by comparison, throw considerable light on the need for competent understanding of the reorientational processes in liquids.

From the experimental point of view the important problem is to separate the individual contributions of the different interactions responsible for relaxation in a liquid. An experimental method for explicit separation of the inter- and intramolecular interaction for proton relaxation is to study the variation of relaxation time as a function of concentration in mixtures of the liquid and its deuterated form^{26,47,48}. Such separations have also been affected by using experimental values of T_1 and known formulae for inter- and intramolecular interactions²⁶. In the present work T_1 and D values measured as functions of temperature are analysed to affect such a separation. The spirit of this work is described briefly in the next section.

I.D Scope of the Present Work

The work presented in this thesis is based on an experimental study of spin-lattice relaxation as a function of temperature in five different liquid systems (i) thiophene (ii) furan (iii) 2-bromothiophene (iv) 3-bromothiophene and (v) 1,2-dichloroethane and is aimed at obtaining the characteristics of molecular motion in these liquids. The experiments were performed on a spin-echo spectrometer operating at 9.78 MHz fabricated for this purpose. The temperature for different liquids ranged from room temperature upto $\sim 40^\circ\text{K}$ below the critical temperature or the temperature at which they might decompose.

In the analysis of the data the contribution of the intermolecular dipolar interaction is separated from the observed relaxation rate by explicitly determining the coefficient of self-diffusion D , in situ, of the sample as a function of temperature. An accurate measurement of D is afforded easily by the spin-echo method⁴⁹. The use of some additional data on density and viscosity along with D values allows a fairly correct estimate of this contribution.

All the molecules studied contain several spins all of which do not necessarily experience intramolecular dipolar interactions of the same strength. When this feature is included in the general theory of relaxation by dipolar interaction one finds that the T_1 -decay is usually given by multiple exponentials due to cross-relaxation effects^{50,51}. The actual decays observed in the experiments are, however, single exponentials. This is explained by the fact that the other time constants have amplitudes too small to be observed. Nevertheless, a detailed consideration of the cross-relaxation effects in the present analysis led to expressions for relaxation rates that are not linear superpositions of the contributions of the individual mechanisms.

The intramolecular contribution to relaxation obtained in this manner is analysed to determine the reorientational parameters in these molecules as a function of temperature. The salient features of these results are given below.

The experimental results on thiophene and furan fall in a similar pattern and show a maximum in the T_1 vs $10^3/T$ curve

which is a clear indication of spin-rotation interaction being present as a mechanism of relaxation for both these compounds. The analysis of the intramolecular relaxation rate in terms of the theory of anisotropic rotational diffusion is simplified by assuming that τ_J , the angular velocity correlation time, is isotropic. This relates the three principal diffusion constants through the respective moments of inertia. With this assumption and the known data on molecular structure, the temperature dependence of D_{\perp} , the rotational diffusion constant perpendicular to the plane of the molecule (both these molecules are planar) and τ_J are determined for both molecules. Furthermore, the spin-rotation interaction constants have been estimated. The results indicate that the molecular reorientation in these systems show deviations from diffusional character at high temperatures.

For 2- and 3-bromothiophenes the T_1 vs $10^3/T$ curves, however, give no indication, of the presence of spin-rotation interaction. The intramolecular relaxation rate is, therefore, entirely due to internal dipolar interactions. The temperature dependence of the rotational correlation times has been derived for both these molecules and are seen to be quite different from each other. The analysis of the data on these molecules, however, required several assumptions regarding the structural and motional constants since these are not available in literature. The contrast in the variation of τ_r for the two cases ~~is~~, even after allowing for this, ^{is} unmistakable.

In 1,2-dichloroethane the intramolecular relaxation rate shows a very small variation with temperature. The reorientational motion of this molecule has the additional complication that the CH_2Cl groups undergo hindered rotation about the C-C bond while the entire molecule tumbles. The rotamer exchange, however, does not seem to be an effective mechanism for modulating the dipolar interactions. The variation of relaxation rates with temperature indicates that the molecular reorientation in this case is predominantly inertial in character.

The material in this thesis is organized in the following manner: The theoretical framework for the analysis of experimental results is sketched in Chapter II. This includes the development of macroscopic differential equations on the basis of the density matrix theory, features of the relaxation mechanisms in liquids, derivation of the relevant correlation functions of molecular motion and a discussion of cross-relaxation effects leading to multiple-exponential relaxation decays.

The spin-echo apparatus fabricated by the author for this work is described in Chapter III. This contains the principle of the method, discussion of the essential circuitry, performance of the equipment, methods of measurement of relaxation times and diffusion constants, a description of the temperature variation accessory and details of sample preparation.

Chapter IV, V and VI contain the experimental results and their analysis, on thiophene and furan, 2- and 3-bromothiophenes and 1,2-dichloroethane respectively.

The important conclusions of this work are summarized briefly in Chapter VII.

This thesis has three appendices, namely, (i) Temperature dependence of the coefficient of self-diffusion in liquids, (ii) Additional details of the spin-echo apparatus, and (iii) Measurement of T_2 by Carr-Purcell method.

Chapter II

THEORETICAL FRAMEWORK

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THEORETICAL FRAMEWORK

In this chapter the basic theoretical framework used in the analysis of the experimental results obtained in this work is described. In Sec. IIA the equations of motion of the magnetization are developed on the basis of the density matrix theory to obtain rigorous expressions for T_1 in terms of the correlation functions of molecular motion. Section II.B sketches the theoretical features of the important mechanisms of relaxation. The calculation of the relevant correlation functions on the basis of specific models for molecular motion, along with expressions for the correlation times used in later chapters is given in Sec. II.C. Finally, in Sec. II.D the case of multi-spin systems in which different groups of spins experience intramolecular dipolar interaction of different strengths, leading, in principle, to multiple-exponential relaxation decays, is considered.

II.A Density Matrix Theory; Macroscopic Differential Equations

A brief discussion of the density matrix formalism for nuclear induction due to Wangsness and Bloch¹³ is given below in order to develop the equations of motion of the magnetization and expressions for the relaxation rates. The procedure followed is essentially that given by Abragam⁷ and what is given below is for the purpose of introducing the notation and some of the relevant physical assumptions. The equation of motion for the

density matrix ρ of the system (spin and lattice) is given by

$$\frac{d\rho}{dt} = -i[\bar{H}_0 + F + H', \rho], \quad (\text{II.1})$$

where H_0 , F and H' refer to the spin hamiltonian, the hamiltonian of the lattice and the spin-lattice interactions all expressed in angular frequency units. Transforming to an interaction representation such that

$$H'^*(t) = e^{iH_0 t} e^{iFt} H' e^{-iFt} e^{-iH_0 t} = e^{iH_0 t} H'(t) e^{-iH_0 t} \quad (\text{II.2})$$

$$\rho^*(t) = e^{iH_0 t} e^{iFt} \rho e^{-iFt} e^{-iH_0 t}, \quad (\text{II.3})$$

gives

$$\frac{d\rho^*}{dt} = -i[H'^*(t), \rho^*]. \quad (\text{II.4})$$

Integrating Eq. (II.4) in two successive approximations and differentiating with respect to time we have

$$\frac{d\rho^*}{dt} = -i[H'^*(t), \rho^*(0)] - \int_0^t [H'^*(t), [H'^*(t-\tau), \rho^*(0)]] d\tau. \quad (\text{II.5})$$

Higher order terms are neglected assuming the relaxation to be weak. If the lattice is assumed to be in thermal equilibrium at $t = 0$, $\rho^*(0)$ is factorizable into spin and lattice parts.

A spin density matrix σ is defined through the relation

$$\sigma = \text{Tr}_f\{\rho\} \quad \text{and} \quad \sigma^* = \text{Tr}_f\{\rho^*\}, \quad (\text{II.6})$$

where $\text{Tr}_f\{\}$ represents a trace over the lattice states.

Equation (II.6) implies

$$\sigma^* = e^{iH_0 t} \sigma e^{-iH_0 t}. \quad (\text{II.7})$$

This leads to

$$\frac{d\sigma^*}{dt} = - \text{Tr}_f \left\{ \int_0^t d\tau [H'(t), [H'(t-\tau), \lambda_0^* \sigma^*(0)]] \right\}. \quad (\text{II.8})$$

λ_0^* is the equilibrium density matrix for the lattice states given by

$$\lambda_0 = \frac{\exp(-\hbar F/kT)}{\text{Tr}_f \{ \exp(-\hbar F/kT) \}}, \quad (\text{II.9})$$

and σ_0 is the equilibrium spin density matrix at the lattice temperature given by

$$\sigma^*(0) = \sigma_0 = \frac{\exp(-\hbar H_0/kT)}{\text{Tr} [\exp(-\hbar H_0/kT)]}, \quad (\text{II.10})$$

where k is the Boltzmann constant. The trace over the lattice states for the first term in Eq. (II.5) gives zero due to the particular choice of the time $t = 0$. Equation (II.8) can be further simplified by using the following considerations:

- (i) In the limit of short correlation times τ_c , $\sigma^*(0)$ can be replaced by $\sigma^*(t)$.
 - (ii) For $\tau_c \ll t \ll T_1$ or T_2 the upper limit of integration can be extended to ∞ .
 - (iii) While taking $\text{Tr}_f \{ \}$ high-temperature approximation is made for the spin system which leads to $\sigma^*(t)$ being replaced by $(\sigma^*(t) - \sigma_0)$ and λ_0 coming out of the double commutator.
 - (iv) For liquids the lattice can be described classically and $\text{Tr}_f \{ \}$ after multiplying by λ_0 can be replaced by an ensemble average $\langle \rangle_{av}$. This leads, in the Schrödinger picture, to
- $$\frac{d\sigma}{dt} = -i[H_0, \sigma] - \int_0^\infty d\tau \langle [H'(t), [e^{-iH_0\tau} H'(t-\tau) e^{iH_0\tau}, \sigma - \sigma_0]] \rangle_{av}. \quad (\text{II.11})$$

In liquids containing several spins of the same species the spin hamiltonian H_0 contains the Zeeman interaction of all the spins including their chemical shifts and indirect spin-spin interactions. This leads to fine structure in high resolution nmr spectra⁶. In the present study (using spin-echo method) the nuclear spins are perturbed by strong r.f. pulses and the results may be adequately described by neglecting the chemical shifts and spin-spin coupling constants, such that

$$H_0 = -\omega_0 \sum_i I_z(i). \quad (\text{II.12})$$

It has been stated (see Sec. I.B) that the spin-lattice interaction hamiltonian can be written as

$$H'(t) = \sum_{\mathbf{q}} (-1)^{\mathbf{q}} F^{\mathbf{q}}(t) A^{-\mathbf{q}}, \quad (\text{II.13})$$

where

$$\begin{aligned} F^{\mathbf{q}*} &= (-1)^{\mathbf{q}} F^{-\mathbf{q}}, \\ (A^{\mathbf{q}})^{\dagger} &= (-1)^{\mathbf{q}} A^{-\mathbf{q}}. \end{aligned} \quad (\text{II.14})$$

where the spin operators are expressed in their irreducible form. From Eqs. (II.12) to (II.14) one gets

$$\begin{aligned} e^{-i H_0 \tau} A^{\mathbf{q}} e^{i H_0 \tau} &= A^{\mathbf{q}}(t) = A^{\mathbf{q}} e^{i \mathbf{q} \omega_0 \tau}, \\ e^{-i H_0 \tau} H'(t) e^{i H_0 \tau} &= \sum_{\mathbf{q}} (-1)^{\mathbf{q}} F^{\mathbf{q}}(t) A^{-\mathbf{q}} e^{-i \mathbf{q} \omega_0 \tau}. \end{aligned} \quad (\text{II.15})$$

With this form for $H'(t)$ the correlation functions simplify through the relation

$$\langle F^{\mathbf{q}*}(t) F^{\mathbf{q}'}(0) \rangle_{av} = \delta_{\mathbf{q}\mathbf{q}'} \langle F^{\mathbf{q}*}(t) F^{\mathbf{q}}(0) \rangle_{av}. \quad (\text{II.16})$$

This is known as the "secular approximation"⁷. Equation (II.11) then becomes

$$\frac{d\sigma}{dt} = -i [H_0, \sigma] - \sum_q (-1)^q J^q(q\omega_0) [A^q, [A^{-q}, \sigma_0]] \quad (II.17)$$

where

$$J^q(q\omega_0) = \int_0^\infty d\tau \langle F^{q*}(t) F^q(t-\tau) \rangle e^{-iq\omega_0 \tau} \quad (II.18)$$

The first term in Eq. (II.17) represents Larmor precession and the second term the effect of relaxation on the evolution of the system. For the purpose of calculating the effect of relaxation the first term need not be considered.

For a given spin operator Q the macroscopic observable is given by

$$\langle Q \rangle = \text{Tr} \{ \sigma(t) Q \}. \quad (II.19)$$

The equation of motion of $\langle Q \rangle$ is (from Eq. (II.17))

$$\frac{d\langle Q \rangle}{dt} = - \sum_q (-1)^q J^q(q\omega_0) \text{Tr} \{ [A^q, [A^{-q}, Q]] (\sigma - \sigma_0) \}. \quad (II.20)$$

For example, the equation of motion for $\langle I_z \rangle$ is given by

$$\frac{d\langle I_z \rangle}{dt} = - \sum_q (-1)^q J^q(q\omega_0) \text{Tr} \{ [A^q, [A^{-q}, I_z]] (\sigma - \sigma_0) \}. \quad (II.21)$$

In the "extreme narrowing" limit⁷ $J^q(q\omega_0)$ may be replaced by $J(0)$, independent of both q and ω_0 , leading to

$$\frac{d\langle I_z \rangle}{dt} = - \sum_q (-1)^q J(0) \text{Tr} \{ [A^q, [A^{-q}, I_z]] (\sigma - \sigma_0) \}. \quad (II.22)$$

If the simplification of Eq. (II.22) for a particular mechanism gives an equation of the form

$$\frac{d \langle I_z \rangle}{dt} = - \frac{1}{T_1} (\langle I_z \rangle - I_0), \quad (\text{II.23a})$$

where $I_0 = \text{Tr} (I_z \sigma_0)$, the validity of Bloch equations is verified for that particular mechanism with

$$\frac{1}{T_1} = AJ(0), \quad (\text{II.23b})$$

where A is a constant of proportionality.

II.B Relaxation Mechanisms in Liquids

In this section the various mechanisms which might cause relaxation in liquids are described. It will be seen from the discussion that only some of them are relevant for the liquids investigated.

(1) Dipolar interaction: For a group of spins the hamiltonian for this interaction is given by

$$H'(t) = \sum_{i < j} I(i) \cdot D_{ij}(t) \cdot I(j), \quad (\text{II.24})$$

where D_{ij} is the dipolar interaction tensor between nuclei i and j . The lattice functions are given by

$$F^q = -(4\pi/5)^{1/2} \frac{\hbar \gamma_i \gamma_j}{r_{ij}^3} Y_2^q(\theta_{ij}, \varphi_{ij}), \quad (\text{II.25})$$

where r_{ij} is the internuclear vector and $(\theta_{ij}, \varphi_{ij})$ are its polar angles in a space-fixed frame. The spin operators are given by

$$\begin{aligned}
A_{ij}^{\pm 2} &= \frac{\sqrt{6}}{2} I_{\pm}(i) I_{\pm}(j) \\
A_{ij}^{\pm 1} &= \mp \frac{\sqrt{6}}{2} (I_{\pm}(i) I_z(j) + I_z(i) I_{\pm}(j)) \quad (\text{II.26}) \\
A_{ij}^0 &= (3I_z(i) I_z(j) - \underline{I}(i) \cdot \underline{I}(j)),
\end{aligned}$$

where

$$I_{\pm} = I_x \pm iI_y. \quad (\text{II.27})$$

There can be two types of dipolar interactions: (a) Interactions between two dipoles sitting on the same molecule or intramolecular dipolar interactions. In this case only the reorientation of the molecule need be considered and this modulates the orientation (θ, φ) of the internuclear vector. The correlation time involved is the rotational correlation time τ_r . (b) Interaction between dipoles sitting on two different molecules or intermolecular dipolar interactions. Here the translational motion of the molecules with respect to each other is of relevance and it is the magnitude of the internuclear vector \underline{r} that is modulated because of molecular motion. The correlation time involved is the translational correlation time τ_t .

This mechanism of relaxation gives an important contribution to T_1 in most liquids.

(2) Spin-rotation interaction: This arises due to the interaction of the nuclear spin with the magnetic field produced at its site by the rotation of the molecule. It represents a term bilinear in the coupling of the ~~rotational~~ angular momentum of the molecule with the angular momentum of the electrons and the

coupling of the angular momentum of the electrons with the nuclear spins in a second order perturbation calculation of the energy of a rotating molecule. If the molecular rotation is considered classically this interaction is modulated by changes in the angular velocity of the molecule and the correlation time involved is the angular velocity correlation time $\tau_J^{15,25}$. The form of the interaction hamiltonian is

$$H'(t) = \underline{I} \cdot \underline{C} \cdot \underline{J}(t) = \sum_{\ell=0}^2 \underline{I} \cdot \underline{C}'_{\ell} \cdot \underline{J}'(t) = \sum_{\ell} (-1)^q F'_{\ell}{}^q A'^{-q}, \quad (\text{II.28})$$

with

$$F'_{\ell}{}^q = \sum_{\underline{m}} (-1)^q C(11\ell, m-qqm) C'_{\ell}{}^m J'^{(-m+q)}, \quad (\text{II.29})$$

where

$$\begin{aligned} C'_0{}^0 &= \frac{1}{3} \text{Tr } C' & C'_2{}^0 &= \frac{\sqrt{6}}{2} C'_{zz}{}^{(2)} \\ C'_1{}^0 &= -i \sqrt{2} C'_{xy}{}^{(1)} & C'_2{}^{\pm 1} &= \pm (C'_{xz}{}^{(2)} \pm i C'_{yz}{}^{(2)}) \\ C'_1{}^{\pm 1} &= \mp i (C'_{yz}{}^{(1)} \pm i C'_{xz}{}^{(1)}) & C'_2{}^{\pm 2} &= \frac{1}{2} [(C'_{xx}{}^{(2)} - C'_{yy}{}^{(2)}) \pm 2i C'_{xy}{}^{(2)}] \\ C'_{ij}{}^{(1)} &= \frac{1}{2} (C'_{ij} - C'_{ji}) & C'_{ij}{}^{(2)} &= \frac{1}{2} (C'_{ij} + C'_{ji} - \frac{2}{3} \text{Tr } C' \delta_{ij}) \end{aligned} \quad (\text{II.30})$$

and

$$\begin{aligned} A'^0 &= I'_z \\ A'^{\pm 1} &= \mp \frac{1}{\sqrt{2}} I'_{\pm} \end{aligned} \quad (\text{II.31})$$

In Eq. (II.28) \underline{I} refers to the nuclear spin, \underline{C} is the spin rotation interaction tensor and \underline{J} is the angular momentum of the molecule. Primed quantities are with respect to a molecule-fixed coordinate frame. $C'_{\ell}{}^m$ are components of the irreducible

spherical tensor C_l^m of rank l ($=0,1,2$) contained in C . C_{ij} are the cartesian components of C . $C(l1l, m-q \ qm)$ is a Clebsh-Gordon coefficient. In certain cases this interaction forms an important mechanism of relaxation and will be considered later.

(3) Quadrupolar interaction: The interaction of the nuclear quadrupole moment with the fluctuating electric field gradients at its site is a powerful mechanism of relaxation of nuclei with spin $> \frac{1}{2}$ in liquids⁷. Since the present work is confined to proton spin relaxation this interaction need not be considered any further.

(4) Scalar coupling modulated by

(a) Chemical exchange: This is a bilinear coupling of the type $A\mathbf{I} \cdot \mathbf{S}$ in which the spin \mathbf{S} undergoes chemical exchange. If the chemical exchange time τ_c is much smaller than $1/A$ this coupling becomes a mode of relaxation⁷. The coupling constant jumps randomly between values A and zero corresponding to \mathbf{I} and \mathbf{S} being on the same or on different molecules respectively. There is, however, no reason to believe that such a mechanism contributes to relaxation in the liquids under study.

(b) Rapid relaxation of spin \mathbf{S} : A situation may also arise when the coupling between the spins $A\mathbf{I} \cdot \mathbf{S}$ becomes time-dependent when the spin \mathbf{S} has a strong mechanism of relaxation of its own such that its relaxation time is much shorter than $1/A$. This often arises when \mathbf{S} is a quadrupolar nucleus. The spin \mathbf{I} , therefore, sees a field produced by \mathbf{S} which is a rapidly

fluctuating function of time. This is pertinent in 1,2-dichloroethane due to the coupling between protons and chlorine. However, it can easily be shown that under normal experimental conditions this would contribute only to T_2 and not to T_1 ⁷. We could, therefore, ignore this mechanism also in the analysis of T_1 data of 1,2-dichloroethane.

(5) Anisotropic chemical shift: The Zeeman coupling of a spin I with a dc magnetic field H given by $-\gamma \hbar I \cdot H$ sometimes requires a correction term because of chemical shielding. This is given by $-\gamma \hbar H \cdot \underline{A} \cdot I$ where \underline{A} is the chemical shielding tensor. Because of the molecular tumbling the anisotropic part of the shielding tensor contributes to relaxation⁷. There is, however, no unambiguous evidence, so far, that such a mechanism contributes significantly to relaxation.

II.C On Correlation Functions

In this section the theoretical calculation of correlation functions used in the analysis is described. From Eqs. (II.18) and (II.23b) it can be seen that the relaxation times are given in terms of time correlation functions of stationary random functions of the lattice variables. The time correlation function of $F^Q(x(t))$ is defined as

$$G(\tau) = \langle F^{Q*}(t) F^Q(t+\tau) \rangle_{av}$$

$$= \iint F^{Q*}(x_1, t) F^Q(x_2, t+\tau) p(x_1, t) P(x_1, t; x_2, t+\tau) dx_1 dx_2 ,$$

(II.32)

where x is the lattice variable which changes with time, $p(x_1)$ is the probability of its possessing a value x_1 at time t and $P(x_1, t; x_2, t+\tau)$ is the conditional probability that if x has a value x_1 at time t , it would have a value x_2 at time $(t+\tau)$. $p(x_1)$ is easily obtained by considering a completely random distribution for x at the initial time t ($G(\tau)$ does not depend on t). The problem of calculating $G(\tau)$ then depends on obtaining an expression for the conditional probability $P(x_1, t; x_2, t+\tau)$. As mentioned before the correlation functions required in the present work involve relative translational motion, reorientational motion and angular velocity changes of the molecules. All these will be considered below in the appropriate diffusional limit.

(1) Translational diffusion;

Intermolecular dipolar interaction: Torrey has given a rather general theory of spin relaxation through translational diffusion on the basis of the theory of random flights²⁷. In the limit of small mean flight paths the results of this theory approach those given by the translational diffusion equation

$$\frac{\partial}{\partial t} p(\underline{r}, t) = D \nabla^2 p(\underline{r}, t), \quad (\text{II.33})$$

where D is the coefficient of self-diffusion. The solution of Eq. (II.33) with $p(\underline{r}, 0) = \delta(\underline{r} - \underline{r}_0)$ leads to

$$P(\underline{r}, t; \underline{r}_0, 0) = (8\pi Dt)^{-3/2} \exp \left[-\frac{(\underline{r} - \underline{r}_0)^2}{8Dt} \right], \quad (\text{II.34})$$

noting the fact that we are here interested, not in the case of a molecule diffusing relative to a fixed point, but in identical molecules diffusing with respect to each other. The correlation functions of $F^Q(t)$, given in Eq. (II.25), for intermolecular dipolar interactions are then given by

$$G^Q(t) = \frac{4\pi}{5} \frac{\rho}{M} \frac{n\gamma^4 \hbar^2}{(8\pi Dt)^{3/2}} \iint \frac{Y_2^{Q*}(\Omega_0)}{r_0^3} \frac{Y_2^Q(\Omega)}{r^3} \times \exp \left[- \frac{(\underline{r} - \underline{r}_0)^2}{8Dt} \right] d^3 r_0 d^3 r, \quad (\text{II.35})$$

where n is the number of spins per molecule, M is the molecular weight, ρ is the density of the liquid, and Ω and Ω_0 are the orientations of \underline{r} and \underline{r}_0 respectively. Each molecule is considered as a hard-sphere of radius 'a' with the spin located at its center so that the lower limit ^{for \underline{r} and \underline{r}_0 in} λ the integrals in Eq. (II.35) should be $2a$ instead of zero. With these considerations the correlation function becomes

$$G^Q(t) = \frac{4\pi}{5} \frac{\rho}{M} \frac{n\gamma^4 \hbar^2}{(2a)^3} \int_0^\infty [J_{3/2}(u)]^2 \exp(-\frac{2D}{a^2} u^2 t) \frac{du}{u}, \quad (\text{II.36})$$

where $J_{3/2}$ is a Bessel function and $u = 2a\epsilon$ where ϵ is a variable entering through the Fourier transform of $\exp \left[- \frac{(\underline{r} - \underline{r}_0)^2}{8Dt} \right]$. The spectral density $J(\omega)$ (see Eq. (II.18)) is then given by

$$J^Q(q\omega) = \left[\int_0^\infty [J_{3/2}(u)]^2 \frac{u\tau du}{u^4 + q^2 \omega^2 \tau^2} \right] \frac{4\pi}{5} \frac{\rho}{M} \frac{n\gamma^4 \hbar^2}{(2a)^3}$$

$$= \frac{4\pi}{5} \frac{n\rho}{M} \frac{\gamma^4 \hbar^2}{(2a)^3} \int_0^\infty \frac{[J_{3/2}(u)]^2}{u^3} \frac{\tau du}{1 + q^2 \omega^2 \tau^2 \frac{u^2}{u^4}}.$$

In the extreme-narrowing limit⁷ this gives

$$J(0) = \frac{4\pi}{75} \frac{n\rho}{M} \frac{\gamma^4 \hbar^2}{2aD}. \quad (\text{II.37})$$

If the intermolecular dipolar interaction is the only mechanism of relaxation Eqs. (II.22), (II.23b) and (II.37) give

$$\left[\frac{1}{T_1} \right]_{\text{inter}} = \frac{n\pi}{5} \frac{\gamma^4 \hbar^2}{Ma} \left[\frac{\rho}{D} \right]. \quad (\text{II.38})$$

The above derivation has the limitations that (i) the radial distribution function of the liquid has not been taken into account and (ii) no allowance was made for the fact that the spins are not necessarily at the center of the molecule. These facts have been taken into account by several authors^{28,52}. Both the corrections add to the above relaxation rate and may be significant when taken together. These contributions could not be considered in a meaningful manner for the liquids studied due to lack of data. It is interesting to note, however, that the proton relaxation rate in benzene calculated with the above formula agrees remarkably well with the experimentally determined^{26,43} $(T_1)_{\text{inter}}$. In view of this we shall ignore the correction terms and use Eq. (II.38) in the present analysis.

Further, from the physical nature of the parameter 'a' it is clear that 'a' is not related in any simple manner to the molecular dimensions. It could be considered as the radius of

that 'equivalent sphere' of which if the liquid is composed the macroscopic transport coefficients and other properties are reproduced. If the molecular translation in these liquids is viewed in terms of Stoke's law (which is rigorously valid only for colloidal particles) 'a' is related to D and η through the relation

$$a = \frac{kT}{6\pi\eta D} . \quad (\text{II.39})$$

This reciprocal relationship between D and η as a function of temperature is examined in several liquids for which the data on η is available by measuring D using the spin-echo technique. These results, given in Appendix I, indicate that the constancy of $\frac{D\eta}{T}$ obtains in several liquids, ^{but} the corresponding 'a' has no direct relationship to molecular dimensions.

In the present work it is necessary to have a reasonable estimate of 'a' for the purpose of calculating the contribution of intermolecular dipolar interaction to relaxation. In the absence of any specifically superior method it was done by using Eq.(II.39) whenever the data on η is available and using the experimental D values. This procedure has its obvious shortcomings in view of the discussion given above although the pattern of results that emerged on this basis for the molecules considered indicates that in these cases it has been satisfactory. The best method devised so far for determining intermolecular contribution is by measuring H^1 and D^2 relaxation times in mixtures of compounds and their deuterated analogues. This

procedure is, however, detailed and cumbersome and difficult to use in every case for reasons ^{of} unavailability of compounds. An approximation like the present is then necessary.

(2) Rotational diffusion; Intramolecular interactions:

We shall now consider correlation functions involved in intramolecular dipolar interactions and spin-rotation interactions that arise from molecular reorientation on the basis of the anisotropic rotational diffusion theory given by Huntress¹⁵.

The rotational diffusion equation is given by

$$\frac{\partial}{\partial t} p(\Omega, t) = - \sum_i D_i L_i^2 p(\Omega, t) \quad (\text{II.40})$$

where $p(\Omega, t)$ is the probability that the molecular orientation is given by Ω , at the time t , D_i are the principal diffusion constants and L_i are the angular momentum components of the molecule in the principal axes system of the diffusion tensor. This theory exploits the formal similarity between Eq.(II.40) and the Schrödinger equation for a rigid rotor (with D_i replaced by $\frac{\hbar^2}{2I_i}$, I_i is the corresponding moment of inertia). The conditional probability $P(\Omega_0, 0; \Omega, t)$ then becomes a Green's function⁵³ and can be written in terms of a complete orthonormal set of energy eigenfunctions $\{\psi_n\}$ of the asymmetric rigid rotor as

$$P(\Omega_0, 0; \Omega, t) = \sum_n \psi_n^*(\Omega_0) \psi_n(\Omega) \exp(-E_n t), \quad (\text{II.41})$$

where E_n is the eigenvalue corresponding to ψ_n .

(a) Intramolecular dipolar interaction: The lattice functions $F^Q(t)$ and the spin operator A^Q for this interaction are given in Eqs. (II.24) to (II.27). $F^Q(t)$'s are given in a space-fixed system. It is convenient to express them in a molecule-fixed frame for the purpose of calculating the correlation functions. Denoting the molecule-fixed quantities with primes we have

$$F^Q(t) = \sum_m (-1)^{Q-m} D_{-Q-m}^{(2)}(t) F'^m, \quad (\text{II.42})$$

where $D^{(2)}$'s are the Wigner rotation matrices⁵⁴ of the second rank. The time-dependence is now entirely contained in these $D^{(2)}$ matrices and the spectral density $J(0)$ becomes

$$J(0) = \int_0^\infty d\tau \sum_{m,m'} (-1)^{Q-Q'-m-m'} F'^m F'^{m'}{}^* \langle D_{-Q-m}^{(2)}(0) D_{Q'-m'}^{(2)*}(\tau) \rangle_{av}, \quad (\text{II.43})$$

with

$$\langle D_{-Q-m}^{(2)}(0) D_{Q'-m'}^{(2)*}(\tau) \rangle_{av} = \iint D_{-Q-m}^{(2)}(\Omega_0) D_{Q'-m'}^{(2)}(\Omega) P(\Omega_0, 0; \Omega, \tau) d\Omega_0 d\Omega. \quad (\text{II.44})$$

In Eq. (II.44) the solution of $P(\Omega_0, 0; \Omega, \tau)$ given by Eq. (II.41) may be substituted. The asymmetric rotor eigenfunctions given in Eq. (II.41) may be expanded in terms of a complete set of symmetric rotor eigenfunctions²¹

$$\psi_{\alpha, M}^J(\Omega) = \sum_K a_K^J(\alpha) \varphi_{KM}^J(\Omega), \quad (\text{II.45})$$

where $\varphi_{K, M}^J(\Omega)$ are the symmetric rotor functions well known to be related to the $D^{(J)}$ matrices. Using the orthogonality

properties of the \mathcal{D} matrices gives

$$J(0) = \frac{1}{5} \sum_{m, m'} (-1)^{m'} F^{(1)}(m) F^{(1)}(-m') \sum_{\alpha} \frac{a_m^{(2)}(\alpha) a_{m'}^{(2)}(\alpha)}{E_{\alpha}^{(2)}} \quad (II.46)$$

It may be noted that the molecule-fixed frame chosen here is the principal axis system of the diffusion tensor. Equation (II.46) reduces, for a dipolar interaction between a single pair of identical spins, to

$$J(0) = \frac{1}{5} \frac{\gamma^4 \hbar^2}{r^6} \tau_r, \quad (II.47)$$

where r is the internuclear distance in the correlation function. The rotational correlation time τ_r is given for a planar asymmetric rotor by

$$\tau_r = \frac{3}{4D_R} \left[(D_x + D_s) \cos^2 \varphi + (D_y + D_s) \sin^2 \varphi - \frac{(D_x - D_y)^2}{D_z + D_s} \cos^2 \varphi \sin^2 \varphi \right], \quad (II.48)$$

and for a symmetric rotor by

$$\tau_r = (6D_{\perp})^{-1} \left[1 + \frac{3(D_{\perp} - D_{//})}{(5D_{\perp} + D_{//})} \sin^2 \theta \left(1 + \frac{3(D_{\perp} - D_{//})}{2(D_{\perp} + 2D_{//})} \sin^2 \theta \right) \right], \quad (II.49)$$

where D_x , D_y and D_z refer to the rotational diffusion constants along the x, y and z axes, $D_{//}$ and D_{\perp} to the diffusion constants for motion about and perpendicular to the symmetry axis respectively, (θ, φ) refer to the polar angles of the internuclear vector, $D_R = 3(D_x D_y + D_y D_z + D_z D_x)$ and $D_s = \frac{1}{3} (D_x + D_y + D_z)$. Substituting Eq. (II.47) in Eq. (II.22), evaluating double commutators and comparing with Eq. (II.23b) we have

$$\left[\frac{1}{T_1} \right]_{\text{intra } D, D_s} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_r, \quad (II.50)$$

for the relaxation rate due to the dipolar interaction between a pair of identical spin- $\frac{1}{2}$ nuclei.

(b) Spin-rotation interaction: The $F^{q'}$'s and $A^{q'}$'s for the spin-rotation interaction are given in Eqs. (II.28) to (II.31). The spin operators are transformed to a space-fixed frame using the Wigner D matrices of the first rank¹⁵

$$A_{\text{molecule-fixed}}^{q'} = \sum_{q'} D_{q'q}^{(1)}(\Omega) A_{\text{space-fixed}}^{q'}, \quad (\text{II.51})$$

where Ω represents the Euler angles of the molecule-fixed axes with respect to the space-fixed axes. Using Eqs. (II.28) to (II.31) and (II.22) the equation of motion for $\langle I_z \rangle$ in the extreme-narrowing approximation can be written as

$$\begin{aligned} - \frac{d}{dt} \langle I_z \rangle = & \sum_{\ell, q, k, m, q', m'} (-1)^{m+k} C(11\ell, m-q, q, m) C(11\ell, m'-q', q', m') C_{\ell}^{m, m'} C_{\ell}^{m, m'} \\ & \times \int_0^{\infty} d\tau \langle J'^*(m-q)(0) D_{kq}^{(1)*}(\tau) \\ & \times J'(-m'+q')(\tau) D_{k-q'}^{(1)}(\tau) \rangle_{\text{av}} \text{Tr} \{ [A^{-k}, [A^k, I_z]] (\sigma - \sigma_0) \}. \end{aligned} \quad (\text{II.52})$$

From Eq. (II.52) it is clear that in the calculation of relaxation rate for spin-rotation interaction two types of correlation functions are involved viz. a rotational correlation function arising from the modulation of the elements of C by the molecular rotation and an angular velocity correlation function ($\underline{J} = \underline{I} \cdot \underline{\omega}$ where \underline{I} is the moment of inertia tensor and $\underline{\omega}$ is the angular velocity) which arises from the modulation of \underline{J} due to

angular velocity changes of the molecule. The separation of the total correlation function into a product of two implies the assumption that the orientation changes and the angular velocity changes have no significant correlation. The expression for T_1 is now obtained to be

$$\left[\frac{1}{T_1} \right]_{SR} = \sum_{\ell, k}^{\prime} (-1)^{m+k} C(11\ell, m-q, q, m) C(11\ell, m'-q', q', m') C_{\ell}^{m'} C_{\ell}^{m'} \\ \times \int_0^{\infty} \langle J^{(1)*}(m-q)(0) J^{(1)}(-m'+q')(\tau) \rangle_{av} d\tau \\ \times \int_0^{\infty} \langle J_{kq}^{(1)*}(0) J_{k-q'}^{(1)}(\tau) \rangle_{av} d\tau, \quad (II.53)$$

where \sum' indicates that k takes values $+1$ and -1 . If the angular velocity correlation time τ_J is much shorter than τ_r , the rotational correlation time, the significant correlation function involves only the angular-velocity-dependent terms, so that

$$\left[\frac{1}{T_1} \right]_{SR} = \frac{2}{3} \sum_{\ell, q, m, m'} (-1)^{m+q} C(11\ell, m-q, q, m) C(11\ell, m'+q-q, m') C_{\ell}^{m'} C_{\ell}^{m'} \\ \times \int_0^{\infty} \langle J^{(1)*}(m-q)(0) J^{(1)}(-m'-q)(\tau) \rangle_{av} d\tau. \quad (II.54)$$

Note that Eq. (II.54) is given in the principal axes system of the moment of inertia tensor. It involves cross correlation terms between angular velocity (ω) components. If cross-correlations of the type $\int_0^{\infty} \langle \omega_m(0) \omega_n(\tau) \rangle_{av} d\tau$ with $m \neq n$ (where m and n take values x, y, z) and contribution from off-diagonal elements of the spin-rotation interaction tensor are negligible¹⁵, and remembering that the diffusion constant¹⁷⁻²⁰.

$$D_n = \int_0^{\infty} \langle \omega_n(0) \omega_n(\tau) \rangle_{av} d\tau, \quad (II.55)$$

and in the diffusional limit Eq. (II.55) gives

$$D_i = \frac{(\tau_J)_i kT}{I_i} , \quad (\text{II.56})$$

where $(\tau_J)_i$ is the correlation time for ω_i and I_i is the corresponding moment of inertia, the relaxation rate is given by

$$\left[\frac{1}{T_1} \right]_{\text{SR}} = \frac{2}{3} kT \sum_{i=x,y,z} [C_{ii}^2 - 2C_t(C_{ii} - C_t)] I_i (\tau_J)_i , \quad (\text{II.57})$$

$$= \frac{2}{3} \sum_{i=x,y,z} [C_{ii}^2 - 2C_t(C_{ii} - C_t)] D_i I_i^2 . \quad (\text{II.58})$$

If the reorientational motion is described in terms of the rotational analogue of the classical Langevin equation^{25,41} given by

$$\dot{\underline{N}} = -\underline{\xi} \cdot \underline{\omega} + \underline{N}'(t) , \quad (\text{II.59})$$

where \underline{N} is the torque experienced by the molecule, $\underline{\xi}$ is the rotational friction tensor and $\underline{N}'(t)$ is a fluctuating torque arising from the changes in the molecular environment, it can be shown that the angular velocity correlation time (neglecting the cross terms in the corresponding Euler's equations) is given by

$$(\tau_J)_i = \frac{I_i}{\xi_i} , \quad (\text{II.60})$$

which relates it to the elements of the friction tensor.

Further, it can be shown that ξ_i are related to the inter-molecular potential through

$$\xi_i = \frac{2I_i}{\pi} \left\langle \frac{\partial^2 V(\mathbf{R}^N)}{\partial \theta_i^2} \right\rangle_{\text{av}} , \quad (\text{II.61})$$

where $V(\underline{R}^N)$ is the potential energy of N molecules in terms of all the relative position vectors. Equations (II.60) and (II.61) serve to interpret the angular velocity correlation time.

The Onsager criterion¹⁵ for the motion of a molecule in a liquid to be diffusional is given in terms of the ratio of the time period for a free rotor (τ_f) to τ_J

$$\chi_i = \frac{1}{6} \left[\frac{\tau_f}{\tau_J} \right]_i = \frac{1}{6D_i} \left[\frac{kT}{I_i} \right]^{\frac{1}{2}} \gg 1. \quad (\text{II.62})$$

If many collisions (in which ω changes) occur in one free-rotational cycle the reorientation is likely to be diffusional.

It can be seen from Eqs. ^{(II.48),} (II.50) and (II.58) that the relaxation rates arising from dipolar interaction and spin-rotation interaction have opposite dependences on D_i and therefore opposite dependences on temperature.

II.D Equations of Motion for Multispin Systems

It is well known that the equations of motion of two spins relaxing through their mutual dipolar interaction leads to coupled differential equations for the z -components of the individual magnetizations^{7,50,55}. These can be obtained by using Eqs. (II.22) and (II.24) to (II.27) for two spins \underline{I}_i and \underline{I}_j , to be

$$\begin{aligned} -\frac{d}{dt} \langle I_{zi} \rangle &= 5J(0) [\langle I_{zi} \rangle - I_{oi}] + \frac{5}{2} J(0) [\langle I_{zj} \rangle - I_{oj}], \\ -\frac{d}{dt} \langle I_{zj} \rangle &= \frac{5}{2} J(0) [\langle I_{zi} \rangle - I_{oi}] + 5J(0) [\langle I_{zj} \rangle - I_{oj}], \end{aligned} \quad (\text{II.63})$$

where I_{0i} is the value of $\langle I_{zi} \rangle$ at equilibrium. If the dipolar interaction is intramolecular $J(0)$ is given by (see Eq. (II.47))

$$J(0) = \frac{1}{5} \frac{\gamma^4 \hbar^2}{r^6} \tau_r, \quad (\text{II.64})$$

and if it is intermolecular in origin (See Eq. (II-37))

$$J(0) = \frac{2\pi}{75} \frac{\gamma^4 \hbar^2}{M a} \frac{\rho}{D}. \quad (\text{II.65})$$

When there are several spins in a molecule such equations of motion can be written for the spins involved in every intramolecular and intermolecular dipolar interaction that exists.* It should be noted that in order to write the equations for the intermolecular interaction it is necessary to consider at least two molecules at a time** and that the correlation function is the same for the interaction between any two spins on different molecules. If the relaxation is contributed primarily by intermolecular interaction the equation of motion for all the spin-pairs add up to give a single exponential decay for the total

* In writing these equations cross-correlation between different pairwise dipolar interactions may be neglected since these are shown to contribute a small effect⁵⁶. In a recent calculation⁵⁷, in which anisotropic effects are included, it was shown that these might lead to non-exponential T_1 -decays. From the experimental observation it appears that such effects are not significant for the present problem.

**

This implies that this interaction is operative primarily at the time of molecular collisions which in turn are assumed to be binary in character i.e. some sort of a bimolecular complex is formed during the collision.

magnetization of a multispin system. On the other hand, if the relaxation is only through intramolecular dipolar interactions in a multispin system the equations of motion for all the spin pairs add up to give a single exponential only if all the spins experience intramolecular dipolar interactions of the same strength (e.g. protons in benzene). Normally both the types of interactions contribute and the relaxation decay would then be a single exponential only if all the spins experience intramolecular dipolar interactions of the same strength.

For the purpose of deriving the equations of motion appropriate for a given multispin system it is convenient to group together the spins which experience intramolecular dipolar interactions of the same strength. If a molecule containing N spins which has α such groups containing $n_1, n_2, \dots, n_\alpha$ spins so that

$$n_1 + n_2 + \dots + n_\alpha = N, \quad (\text{II.66})$$

the equation of motion of the total magnetization of the first group due to intermolecular interactions is given by

$$\begin{aligned} -\frac{d}{dt} \langle \sum_{i=1}^n (I_{zi} + I'_{zi}) \rangle &= \frac{15n_1}{2} J(0) \langle \sum_{i=1}^{n_1} \{ (I_{zi} + I'_{zi}) - (I_{oi} + I'_{oi}) \} \rangle_{\text{av}} \\ &+ 5(N - n_1) J(0) \langle \sum_{i=1}^{n_1} \{ (I_{zi} + I'_{zi}) - (I_{oi} + I'_{oi}) \} \rangle_{\text{av}} \\ &+ \frac{5n_1}{2} J(0) \langle \sum_{\beta=2}^{\alpha} \sum_{i=1}^{n_\beta} \{ (I_{zi} + I'_{zi}) - (I_{oi} + I'_{oi}) \} \rangle_{\text{av}} \end{aligned} \quad (\text{II.67})$$

where I_{zi} and I'_{zi} represent the z -components of the spins on the two molecules, $J(0)$ is given by Eq. (II.65). The first term represents the interaction between n_1 spins each on the two molecules and the other two terms represent interactions

between groups. These are referred to as 'cross-relaxation' terms. For the intramolecular interactions, however, the equations would be more complicated, e.g., the equation of motion for the total magnetization of the first group is given by

$$\begin{aligned}
 -\frac{d}{dt} \left\langle \sum_{i=1}^{n_1} I_{zi} \right\rangle = & \sum_{i < j}^{n_1} \{ 2C_{ij}^{11} \langle I_{zi}^1 - I_{oi}^1 \rangle + C_{ij}^{11} \langle I_{zj}^1 - I_{jo}^1 \rangle \} \\
 & + \sum_{i=1}^{n_1} \sum_{\beta=2}^{\alpha} \sum_{j=1}^{n_{\beta}} \{ 2C_{ij}^{1\beta} \langle I_{zi}^1 - I_{oi}^1 \rangle + C_{ij}^{1\beta} \langle I_{zj}^{\beta} - I_{jo}^{\beta} \rangle \} ,
 \end{aligned}
 \tag{II.68}$$

where $C_{ij}^{1\beta}$ is the coefficient, $(5/2)J(0)$, corresponding to the interaction between spin i and j on groups 1 and β respectively. It is clear that a sum of Eqs. (II.67) and (II.68) does not lead to a single exponential decay for the total magnetization of either all the groups or any individual group. Brooks et al⁵⁰ have considered this problem and experimentally demonstrated the existence of two exponentials in the proton relaxation decay of 1-phenylpropyne. Recently similar effects were observed in the three proton system of 1,1,2-trichloroethane⁵⁸.

In Chapters IV to VI we consider multispin systems in which the equations of motion of the above type yield two exponentials. The interpretation of the observed relaxation rates, even if it is a single exponential experimentally, in terms of such equations improves the accuracy in the determination of the relaxation parameters therein.

Chapter III

THE SPIN-ECHO APPARATUS

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THE SPIN-ECHO APPARATUS*

The phenomenon of spin-echos originally introduced by Hahn⁶⁰ has been used to considerable advantage in the study of spin-relaxation. The response of the spin system to specially chosen combinations of strong resonant r.f. pulses leads to the formation of transient resonance signals known as 'echos', characteristic of the coherence in the motion of the spins. Measurements on the echos for specific pulsing arrangements leads to the determination of relaxation times. The principal advantage of this method over the conventional steady-state nmr method is that no r.f. field is required to observe the signals and hence the system is completely unperturbed when the 'spin-echos' are observed. A brief description of the formation of spin-echos and details of the spin-echo apparatus and accessories fabricated for the measurement of relaxation times and coefficients of self-diffusion is given in this chapter.

III.A Formation of Spin Echos

Consider a system of nuclei in a magnetic field given by

$$\underline{H} = H_0 \hat{k} + \Delta H_0(z) \hat{k} + 2H_1 \cos \omega t \hat{i} . \quad (\text{III.1})$$

The first two terms represent a uniform static magnetic field ($H_0 \hat{k}$) along the z-axis superposed by an inhomogeneity ($\Delta H_0(z) \hat{k}$)

*The details of the spin-echo apparatus given in this chapter appear as a Technical Report⁵⁹.

assumed to be along the same axis for simplicity. The last term represents an r.f. field of frequency close to the resonant value. The oscillating field is equivalent to the superposition of two counter-rotating fields

$$H_1(\cos\omega t \hat{i} \pm \sin\omega t \hat{j}). \quad (\text{III.2})$$

The precessional motion due to the first term in Eq. (III.1) may conveniently be described by transforming to a coordinate frame rotating about the z-axis at a frequency $(-\omega \hat{k})$. In this frame the nuclei see an effective field

$$\underline{H}_{\text{rot}} = (H_0 - \frac{\omega}{\gamma}) \hat{k} + \Delta H_0(z) \hat{k} + H_1 \hat{i}. \quad (\text{III.3})$$

The effect of the other rotating field in this frame is negligible. If ω exactly equals the resonance frequency i.e.

$$\omega = \gamma H_0, \quad (\text{III.4})$$

and the r.f. is sufficiently strong such that

$$H_1 \gg \Delta H_0, \quad (\text{III.5})$$

the nuclei essentially precess about the x-axis. Now, if the r.f. field is applied just for a period t_1 such that

$$t_1 \ll T_1 \text{ or } T_2, \quad (\text{III.6})$$

the relaxation terms in Eq. (I.1) may be neglected during this period and the nuclei precess through an angle

$$\theta = \gamma H_1 t_1, \quad (\text{III.7})$$

about the x -axis. Further, if before the application of the r.f. pulse the sample attained a net magnetization $M_0 \hat{k}$ (Fig. 1A)⁴⁹ this vector would also precess about the x -axis through an angle θ (Fig. 1B) in the time t_1 .

Consider the case when t_1 is such that $\theta = \pi/2$. The entire magnetization is now tipped into the xy -plane (Fig. 1C) and the r.f. is off. Then the only field seen by the nuclei is $\Delta H_0(z) \hat{k}$ because of which nuclei at different parts in the sample precess at different rates. A magnetization vector called an 'isochromat'⁶⁰ is associated with all the spins in the sample experiencing the same magnetic field. The inhomogeneity results in a fanning out of these isochromats in the xy -plane (Fig. 1D) leading to a decay of the magnetization in this plane in times of the order of $(\gamma \Delta H_0)^{-1}$. This is known as 'free-induction decay' or the 'tail' of a $\pi/2$ -pulse. The height of the tail is a direct measure of the magnetization along the z -axis prior to the application of the $\pi/2$ -pulse.

The phase dispersion represented by the decay of the 'tail' following the $\pi/2$ -pulse can be reversed by applying a π -pulse at a time τ ($\ll T_1$ or T_2) after the $\pi/2$ -pulse. The effect of this pulse would be to turn the isochromats through an angle π about a direction in the xy -plane (taken as y -axis for simplicity) (Fig. 1E.) and when the pulse is off the isochromats would continue to precess in the same direction as they were before the π -pulse (Fig. 1F). This leads to a reclustering of the isochromats at a time τ after the π -pulse

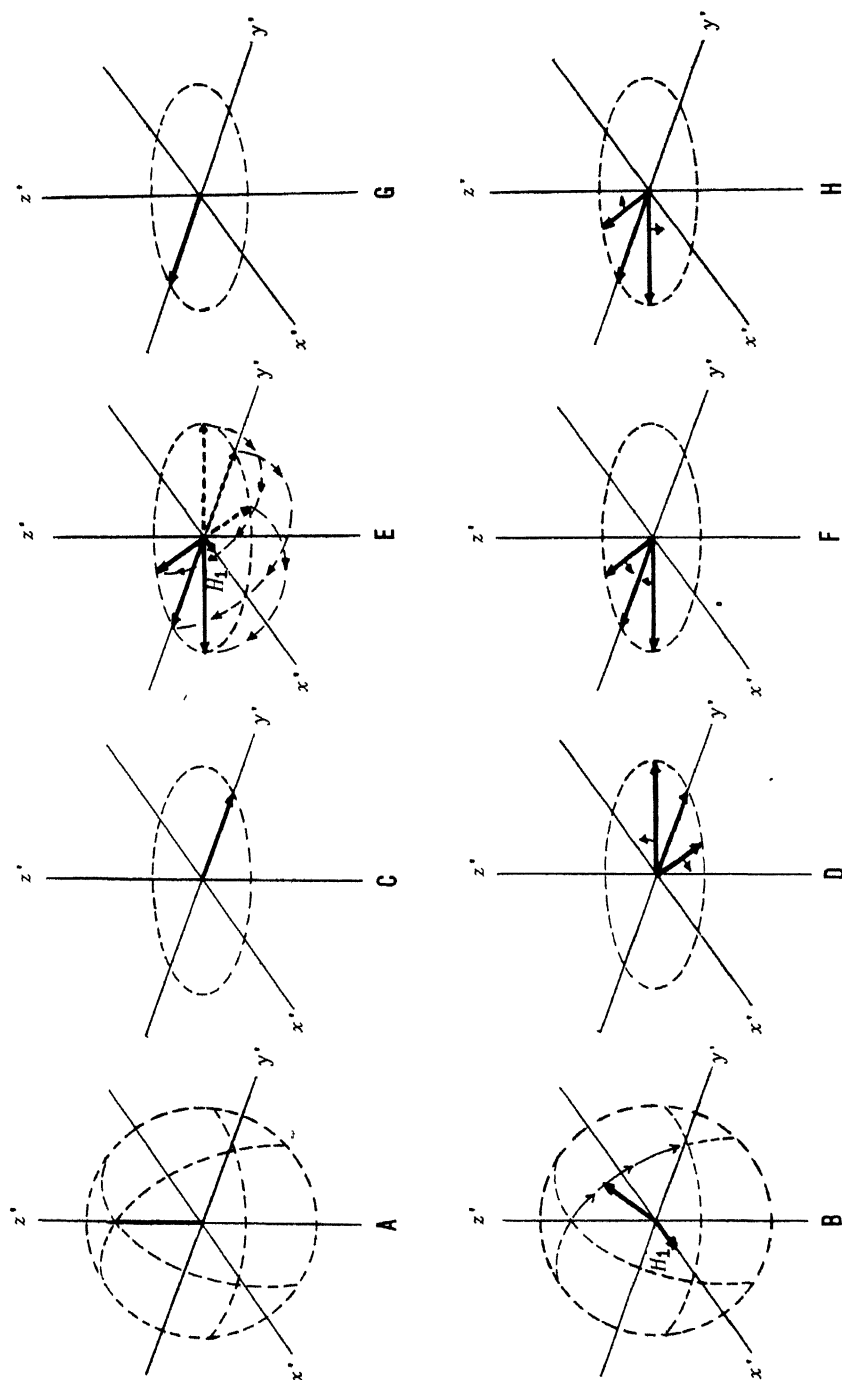


FIG. 1: ECHO FORMATION FOLLOWING A $\pi / 2 - \pi$ SEQUENCE
(Carr H. Y. and Purcell E. M.^{4q})

giving rise to what is known as an 'echo' (Fig. 1G). The height of the echo is proportional to the total magnetization in the xy-plane at that time.

During the time 2τ that elapsed between the initial $\pi/2$ -pulse and the appearance of the echo the relaxation terms in the equation of motion of the individual isochromats will be operative. These terms lead to a shortening of the lengths of the isochromats. Further loss of magnetization during this interval may also result from diffusion of the spins in the inhomogeneous field. The study of the echo for different types of pulsing arrangements is thus capable of yielding information on relaxation and diffusion.

An apparatus to facilitate such a study was fabricated in our laboratory. The salient features of this are described in the next section.

III.B Description of the Apparatus

A spin-echo spectrometer involves an arrangement for applying short intense bursts of r.f. to the sample in the desired sequence. The induced signal after detection and amplification is displayed on an oscilloscope. The block diagram of a spin-echo spectrometer is shown in Fig. 2. The pulse programmer gives the required pulse sequence in the form of dc voltages. These gate a crystal-controlled continuous-wave master oscillator which gives pulsed r.f. to the coil surrounding the sample placed in a magnetic field. The response

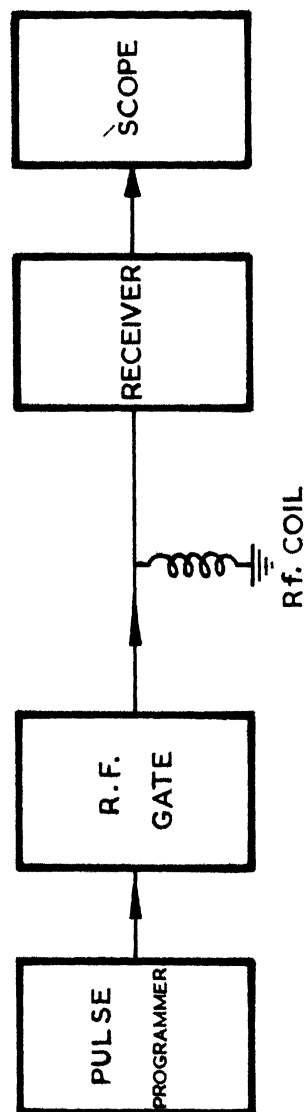


FIG. 2: BLOCK DIAGRAM OF THE SPIN-ECHO SPECTROMETER

of the sample to the disturbance is picked up by the receiver coil, amplified and detected. A description of the different parts of the apparatus is given below. The important circuits are included in this chapter. Some of the routine circuits used are given in Appendix II.

1. Pulse programmer:^{*} The pulse programmer is a combination of Tektronix^{**} waveform generator (Tek 162) and Tektronix pulse generators (Tek 161 and Tek 163) together with some simple electronic circuits designed to give the required sequence of pulses. Explicit description of some of the important pulse sequences is given in Sec. IIIC.

2. Gated Oscillator:^{*} The gated oscillator supplies r.f. power of controllable amplitude and duration to the r.f. coil when subjected to dc pulses from the pulse programmer. Since at all other times there should be no r.f. reaching the sample coil the carrier suppression ratio should be infinite. In practice this is not obtainable due to obvious limitations of electrical circuits. A gated oscillator with a carrier suppression ratio $\geq 10^9$ designed by Blume⁶¹ and modified by Proctor⁶² has been used in this apparatus (see Fig. 3.).

*

We were benefitted by some consultations with Drs. K. Lalita and K.V.L.N. Sastry in constructing these.

**

Tektronix Inc., Beaverton, Oregon, U.S.A.

A crystal controlled oscillator operating at 9.78 MHz is used to provide continuous-wave r.f. voltage of about 5 volts at the cathode of an isolation stage (1/2 6DJ8). The crystal (HC-6^{*}) is housed in an oven (HO-9^{*}) and maintained at 85°C by thermostat control for frequency stability. The isolation stage is coupled to the cathode of a 7077 held cut-off by applying (-12V) at its plate. 7077 is a cylindrically symmetric tube whose planar grid forms a perforated region in the lid of a copper can which shields the entire oscillator circuitry. Any leakage r.f. which may reach the plate of 7077 because of its interelectrode capacitance is bypassed to ground through the low dynamic impedance of a conducting diode IN307.

The dc pulses arranged in the required sequence are fed to one of the grids of a duo-triode (12AT7). Limitations on the amplitudes of the pulses obtainable from Tektronix pulse generators necessitate the addition of this stage to Blume's circuit. D.C. pulses amplified to about 90 volts swing the plate of 7077 positive. The bypass diode is back biased, 7077 conducts and r.f. of about 20 volts peak to peak reaches the power amplifiers through a voltage divider and an isolation stage (1/2 5687). At the grid of the power amplifiers there is another diode which grounds any leakage r.f. Two 5763's connected in parallel are used as power amplifiers to give about 300 volts peak to peak of pulsed r.f. These tubes have a tendency to pick up r.f. noise and, therefore, need good shielding.

* From International Crystal Manufacturing Company, Oklahoma, Oklahoma, U.S.A.

3. Radio-frequency receiver: The r.f. receiver is an amplifier-detector system based on a circuit sent to us by Proctor* (see Fig. 4). Four identical stages, 6AK5's, each of which has an amplification factor of about 10, form the pre-detection amplifiers. In a spin-echo experiment one is usually interested in detecting signals of short duration δ ($20\mu\text{sec} \leq \delta \leq 1 \text{ msec}$) and it, therefore, becomes necessary to broadband the receiver. Stagger-tuning the amplifier in pairs gives a bandwidth of about 1MHz (3 db down) for the tuning range of 8-20 MHz. This places a limitation on the net gain of the receiver since the gain bandwidth product is constant. The amplified signal is detected by a diode (OA5), the output is amplified by a 12AX7 and can be displayed on an oscilloscope. The net gain achieved is 10,000 with a signal to noise ratio of 2:1 for 80% modulation at 3 μ v carrier voltage. Since we are using a single coil probe the receiver is subjected to intense r.f. pulses which saturate it. It is, therefore, essential to have a short recovery time if the actual decay is to be observed. This receiver has a recovery time of about 15 μsec and accepts a maximum input signal of 300 μvolts .

* We thank Dr. W.G. Proctor, Varian Associates, Palo Alto, California, U.S.A. for sending us the circuits of the receiver and gated oscillator used by him⁶².

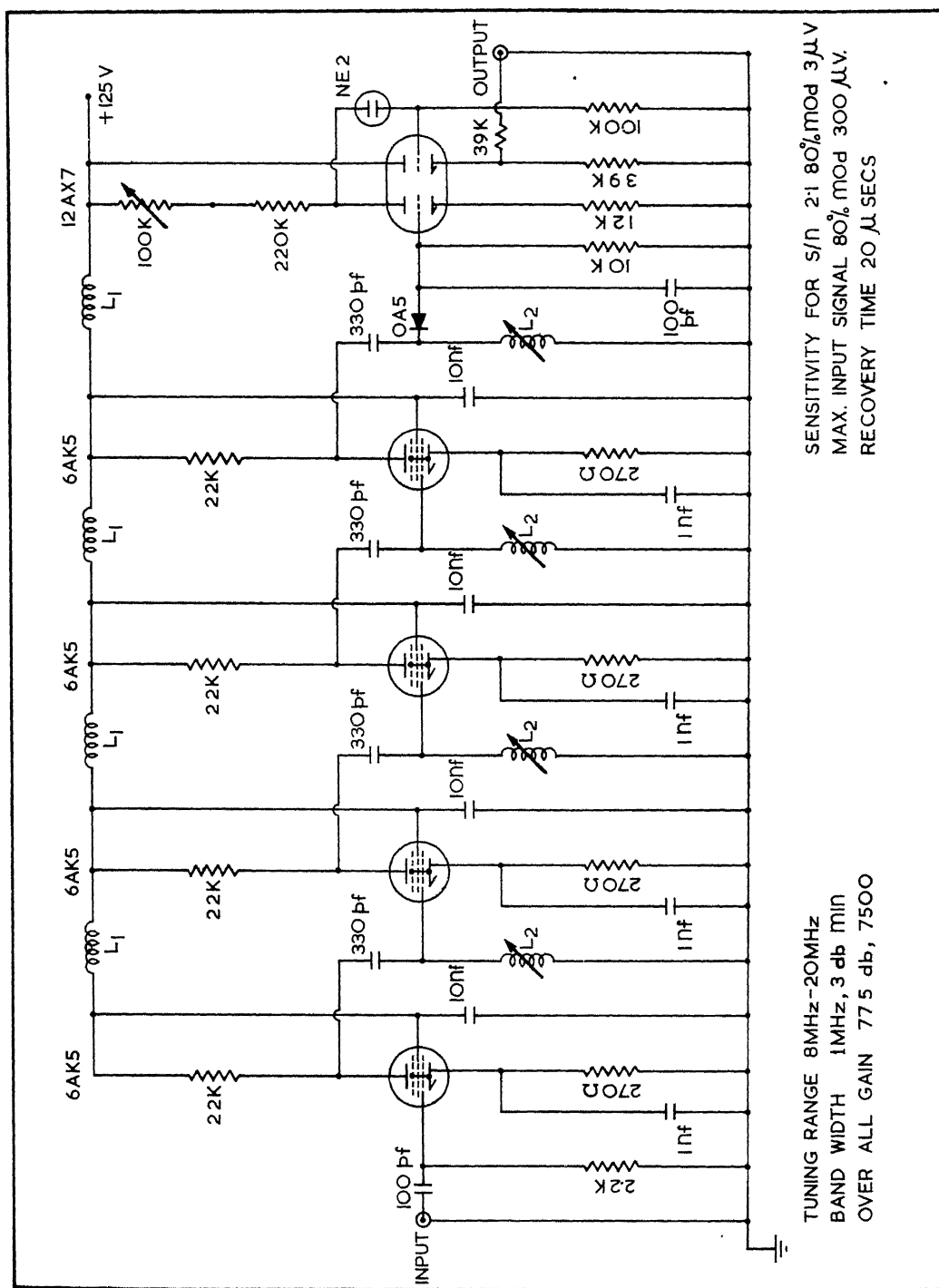


FIG. 4 : RADIO FREQUENCY RECEIVER

To avoid oscillations the amplification stages are shielded from each other and the components arranged to minimize pick up. L_2 are high Q (=80) coils honey-comb wound on a ceramic former with a ferrite core.

The receiver was tested for linearity for output signals ranging from 0.5 volts to about 6.0 volts. The signal strengths obtained for different samples plotted against density of spins yield a straight line passing through the origin.

4. Other accessories: The probe is described as part of the temperature variation accessory.

The magnet^{*} used is a Varian^{**} Model V-3800 15" magnet with a V-FR2703 power supply.

The signal is displayed on a Tektronix 564 Storage Oscilloscope[†] together with Type 3A3 plug-in unit.

The time intervals were measured using a Hewlett-Packard^{††} 5245M Electronic Counter equipped with a 5262A Time Interval Unit.

* We thank the Low Temperature Group of I.I.T. Kanpur for permitting the use of their magnet. The early testing of the spectrometer was done on a Polytronic (Polytronic Inc., Bombay, India) electromagnet loaned by Professor P.T. Narasimhan, Department of Chemistry, I.I.T. Kanpur.

** Varian Associates, Palo Alto, California, U.S.A.

† We thank the Hydraulics Group, Department of Civil Engineering, I.I.T. Kanpur for loaning us this Oscilloscope.

†† Hewlett-Packard Inc., Palo Alto, California, U.S.A.

III.C Details of Performance

1. Typical pulse sequences: The arrangement⁶³ for obtaining a three pulse sequence is shown in Fig. 5.

A Tektronix waveform generator (Tek 162), triggered manually, gives a sawtooth and a pulse (a) at the beginning of each sawtooth. The sawtooth is used to trigger a Tek 161 pulse generator which in turn gives a positive pulse ($\sim 25V$) of adjustable width. This pulse is fed to a differentiator-inverter circuit to obtain two positive spikes (b) and (c). (a) and (b) are fed to a mixer the output of which triggers a Tek 163 pulse generator and (c) is fed to another Tek 163 to obtain a set of three dc pulses. The interval between (b) and (c) can be adjusted by altering the width of the Tek 161 pulse. The interval between (a) and (b;c) can be varied by changing the point on the sawtooth at which Tek 161 is triggered. The arrangement shown is for a three-pulse sequence in which the first two pulses have the same width (e.g. a $\pi/2-\pi/2-\pi$ sequence used for T_1 measurement). The output of the two Tek 163's are mixed and inverted and used to gate the master oscillator. To obtain a two-pulse sequence (e.g. a $\pi/2-\pi/2$ or $\pi/2-\pi$ or $\pi-\pi/2$) the initial trigger (a) is eliminated.

Typical series of two and three r.f. pulses are shown in Figs. 6 and 7 respectively.

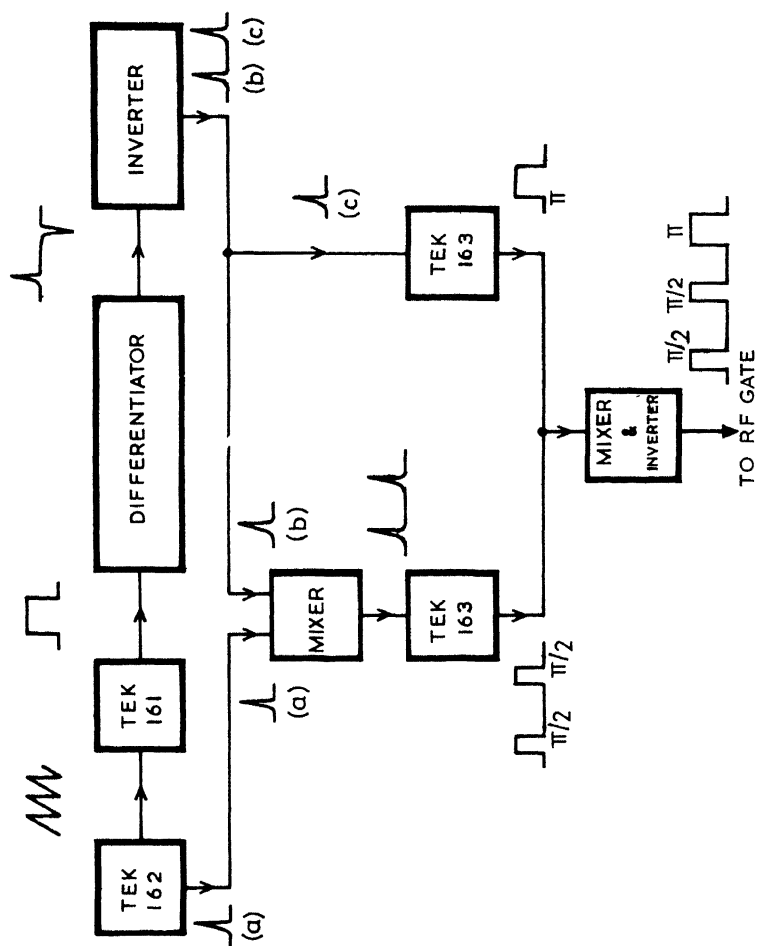


FIG. 5: BLOCK DIAGRAM FOR OBTAINING A THREE PULSE SEQUENCE.

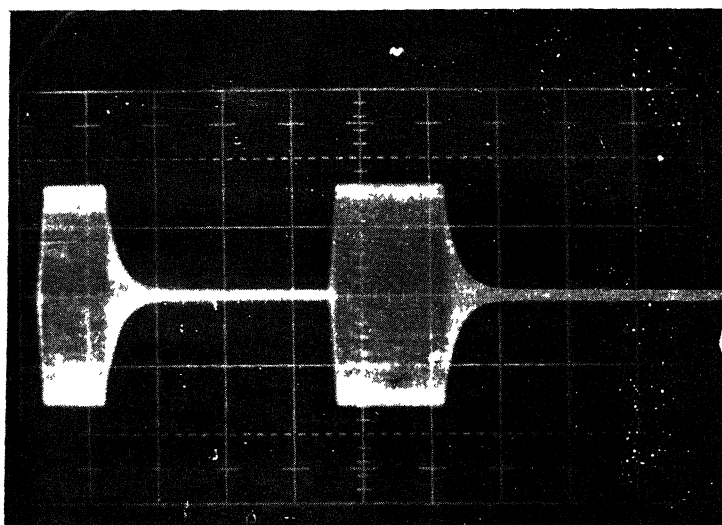


FIG. 6 : A TWO PULSE SEQUENCE

(Pulse widths: 10μ secs and 20μ secs; Pulse separation: 60μ secs.)

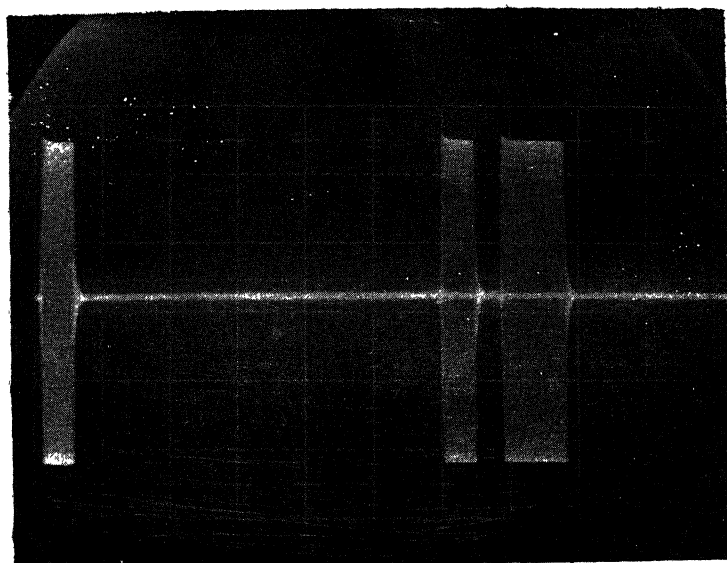


FIG. 7: A THREE PULSE SEQUENCE (Pulse widths: 10μ sec, 10μ sec, 20μ sec;
Pulse separation: 60μ sec, 12μ sec).

(2) Signals obtained: It has been explained in Sec. III.A that a sequence of a $\pi/2$ - π pulses leads to the formation of an echo. Adjustments for $\pi/2$ and π pulses can be made using a procedure given by Schwartz⁶⁴. Figure 8 shows a tail following a $\pi/2$ -pulse in glycerine. An echo, following a $\pi/2$ - τ - π sequence, in glycerine is shown in Fig. 9.

III.D Measurement of Relaxation Times and Diffusion Constants

(1) T_1 measurement: One can employ several pulse sequences for measuring T_1 e.g. $\pi/2$ - $\pi/2$; π - $\pi/2$; $\pi/2$ - $\pi/2$ - π etc. The $\pi/2$ - $\pi/2$ - π method is described here. An initial $\pi/2$ -pulse tips the equilibrium magnetization into the xy-plane. A $\pi/2$ - τ - π sequence applied t seconds later monitors the magnetization that has developed along the z-axis during that interval. The height of the echo appearing a time τ after the π -pulse would be a measure of this magnetization and hence the time τ ($\ll T_1$ or T_2) should be kept constant (about 0.6 msec in our experiments) throughout the experiment. The rate of growth of magnetization along the z-axis is determined by measuring the height of the echo as a function of t . The time constant of this growth gives T_1 . t can be varied from a fraction of a second upto over a hundred seconds depending on the value of T_1 being measured. The error in T_1 measurement is about $\pm 5\%$.

(2) D measurement: The discussion of spin-echos in Sec. III.A is based on the assumption that the spins are always

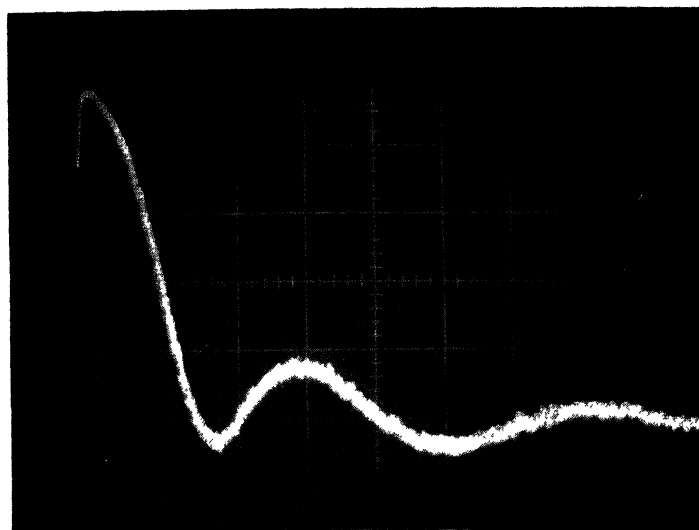


FIG. 8 : TAIL FOLLOWING A $\pi/2$ - PULSE
(X axis: 1.0 m sec/cm)

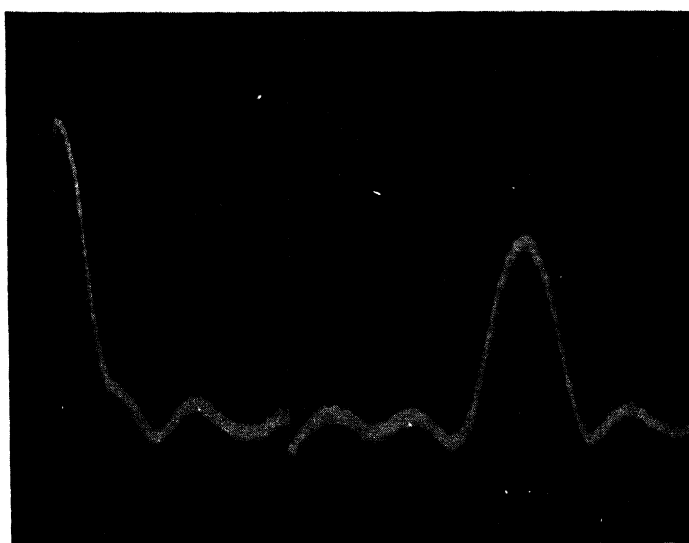


FIG. 9 : ECHO FOLLOWING A $\pi/2$ - τ - π PULSE SEQUENCE
(X axis: 2.0 msec/cm
Pulse width: 3.7μ secs and 7.0μ secs.)

located at the same value of the magnetic field so that their precession frequencies remains constant. The height of the echo would then be a measure of the decay of magnetization in the xy-plane during the interval 2τ because of relaxation. In actual practice, however, spins diffuse through an inhomogeneous field and thereby undergo changes in their precessional frequencies as a function of time. There would, therefore, be an additional dephasing of the isochromats arising from self-diffusion of the molecules containing the spins thereby causing a decay in echo amplitudes much faster than that due to relaxation. Carr and Purcell have shown that this decay is not an exponential, but has the form^{7,49}

$$M(t) = M(0) \exp\left(-\frac{t}{T_2} - \frac{D\gamma^2 G^2 t^3}{12}\right), \quad (\text{III.8})$$

in a magnetic field of constant gradient G along the z -axis, where $M(t)$ is the echo amplitude at any time t .

In all the liquids considered the $\exp(-t/T_2)$ decay was very slow because of large relaxation times and was completely swamped by the diffusion decay so that the first term in the exponential may be ignored. A plot of $\log \frac{M(t)}{M(0)}$ versus t^3 gives D provided G is known.

A constant gradient was obtained across the sample by keeping it in a homogeneous field and superposing on it a gradient obtained by using two circular rings of current, placed symmetrically with respect to the r.f. coil, with their axis along the homogeneous field direction. The coils were of about

50 turns each of No. 20 enamelled copper wire wound on perspex formers ~ 7.0 cms in diameter and placed 5.5 cms apart.

The gradient was determined by a procedure described by Douglass and McCall⁶⁵ based on the measurement of echo shape. The shape of the echo at resonance for a cylindrical sample with its axis perpendicular to the gradient direction is given by

$$\frac{J_1(\gamma Gta/2)}{\gamma Gta/2} , \quad (\text{III.9})$$

where 'a' is the diameter of the sample and $J_1(\gamma Gta/2)$ is a Bessel function of first order. An echo shape for a gradient of 0.2 gauss/cm is shown in Fig. 10. The two first minima of the echo shape on either side of the central maxima are separated by an interval t such that

$$\gamma G = \frac{20.54}{at} , \quad (\text{III.10})$$

from which G may be determined. This value agrees with that determined from the known values of D for H_2O ⁶⁶. For the coils used a gradient of 1.55 gauss/cm is obtained for a current of 100 mAs. The error in the D values measured is about $\pm 5\%$.

Carr and Purcell⁴⁹ suggested a method of determining T_2 by using $\frac{\alpha}{2}\pi$ -pulse followed by a series of π -pulses. This largely reduces the effect of diffusion on the decay. The spectrometer used is constructed to make T_2 measurements also. Since T_2 measurements are not used in this work, the details of this are described in Appendix III.

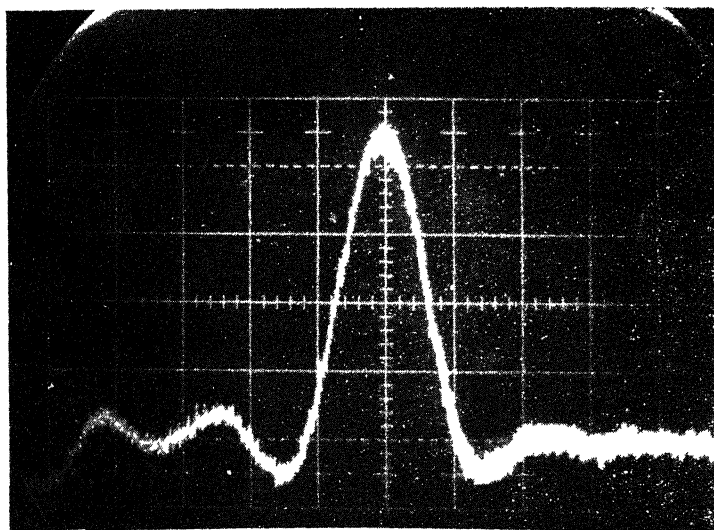


FIG. 10 : SHAPE OF AN ECHO IN GLYCERINE
(X axis = 2 m secs/cm.)

III.E Variable Temperature Probe

A cryostat suitable for relaxation studies from liquid nitrogen temperature upto 600°K was constructed* on the basis of a design by Gutowsky ⁶⁷et al. It consists of a silvered glass dewar which contains a brass coolant chamber, heater coils and a probe which fit inside the dewar. A cross section of the assembly is shown in Fig. 11.

The probe consists of a split copper block 3.0 cms in diameter. The lower half serves merely to hold the sample. The upper half in addition to holding the sample supports the heater coils and the heat leak. The heater coils consist of about 2.5 meters of No.27 double-silk-insulated Eureka wire wound on two copper spools about 3 mm in diameter. These coils have a resistance of about 30Ω each and are connected in parallel. They are heated by current supplied from an APLAB** regulated D.C. power supply. The heat leak is a 20 cm long brass-copper rod which forms a direct thermal contact between the copper block and the coolant chamber. There is a 10 cm long copper sleeving which can be moved over the brass part of the rod thereby controlling the amount of brass in

* We thank Professor T.M. Srinivasan, Department of Physics, I.I.T. Kanpur, for suggestions regarding the construction of this probe.

** Applied Electronics Ltd., Thana, Maharashtra, India

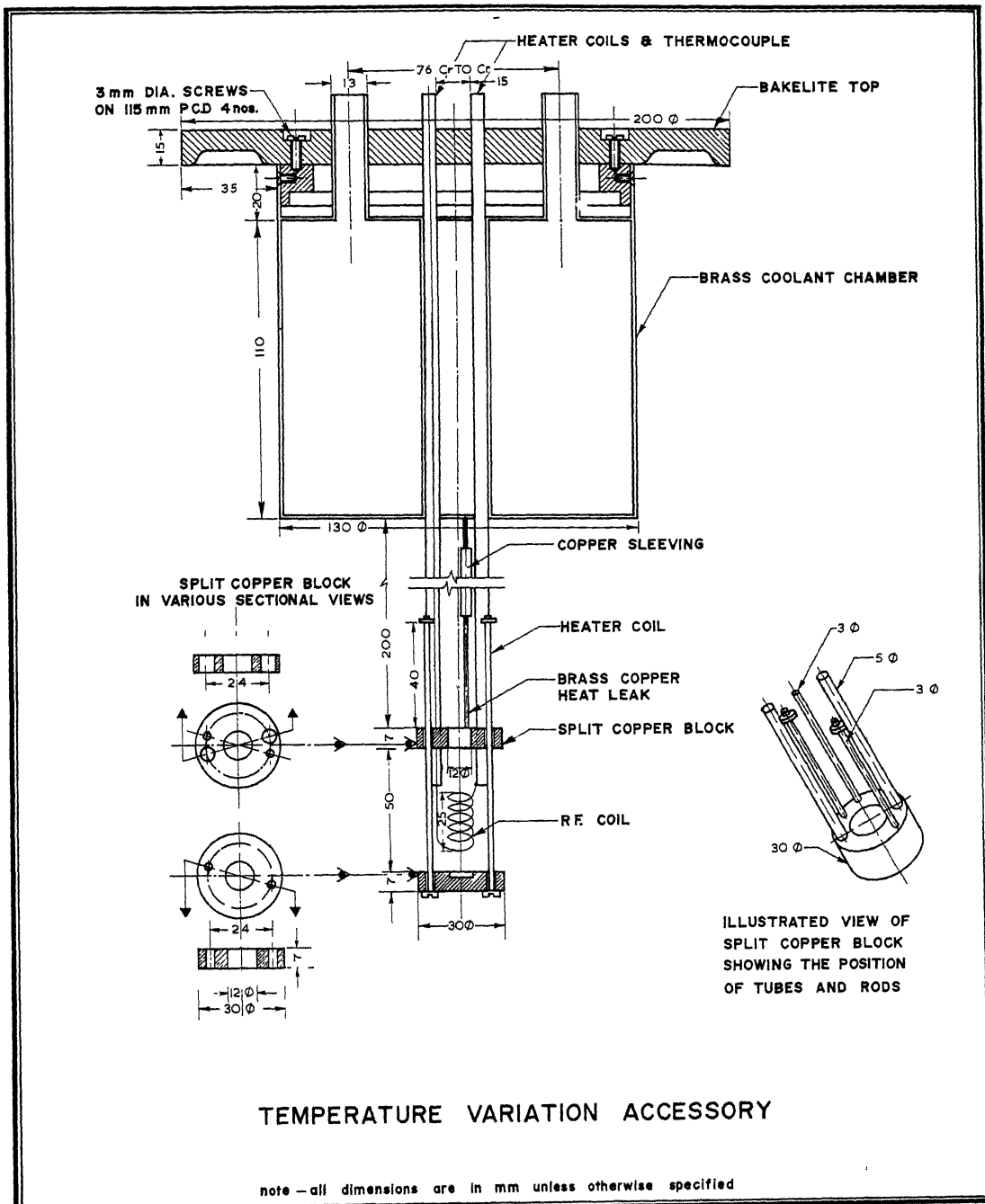


FIG. 11 :

the circuit. Electrical connections to the power supply are made through a brass tubing, 5mm o.d., which extends from the copper block to the top of the dewar. Another thin walled brass tubing with teflon spacers serves as an r.f. coaxial cable to the sample coil which lies between the two copper blocks. The coolant chamber is an annular brass structure with its inner and outer diameters as 3 cms and 13 cms respectively and about 11 cms in height and can be filled with the coolant. The temperature is measured with a copper-constantan thermocouple one end of which sits in the sample tube. The voltage is measured with a Leeds and Northrup* 8687 volt potentiometer. Temperatures ranging from room temperature upwards were obtained by using the heater coils only. The current required for the maximum temperature was of the order of 1.0 amp. Re-equilibrium on increasing the heater current was established within 45 minutes. The temperature was stable to within a degree over long periods.

III.F Sample Preparation

The samples were contained in pyrex glass tubes 1 cm o.d. and about 10 cm in length. In all the cases the experiments were performed along the liquid-vapor equilibrium curve by filling the sample tubes in a calculated ratio of liquid to vapor at room temperature. This ratio is given by

$$\frac{V_L}{V_V} = \frac{\rho_C}{\rho_R} \quad , \quad (\text{III.11})$$

* Leeds and Northrup Inc. North Wales, Pennsylvania, U.S.A.

where V_L and V_V refer to volume of liquid and vapor at room temperature and ρ_C and ρ_R to the critical temperature and room temperature densities respectively. The r.f. coil essentially covers the region of the liquid at room temperature. A picture of the sample tube before sealing is shown in Fig. 12. A constriction was made between the liquid and vapor phases at room temperature to avoid the effect of diffusion on T_1 measurements. A small cavity was made near the base of the tube to support the thermocouple. A tube containing electrodes fixed with a barium getter^{*} was attached to the main body of the sample tube.

'Analar' grade chemicals^{**} were first fractionally distilled^{***} at atmospheric pressure. Dissolved oxygen was removed by first flushing the sample with nitrogen and then subjecting it to six or more freeze-pump-thaw cycles (at a pressure ~1 micron of Hg) and sealing at the top constriction. The getter was then fired following a procedure similar to that given by Moniz et al.³⁰ The sample was then sealed at the second constriction. This sample was contained in the r.f. coil and good thermal contacts were ensured to minimize temperature gradients thereby reducing convection effects.

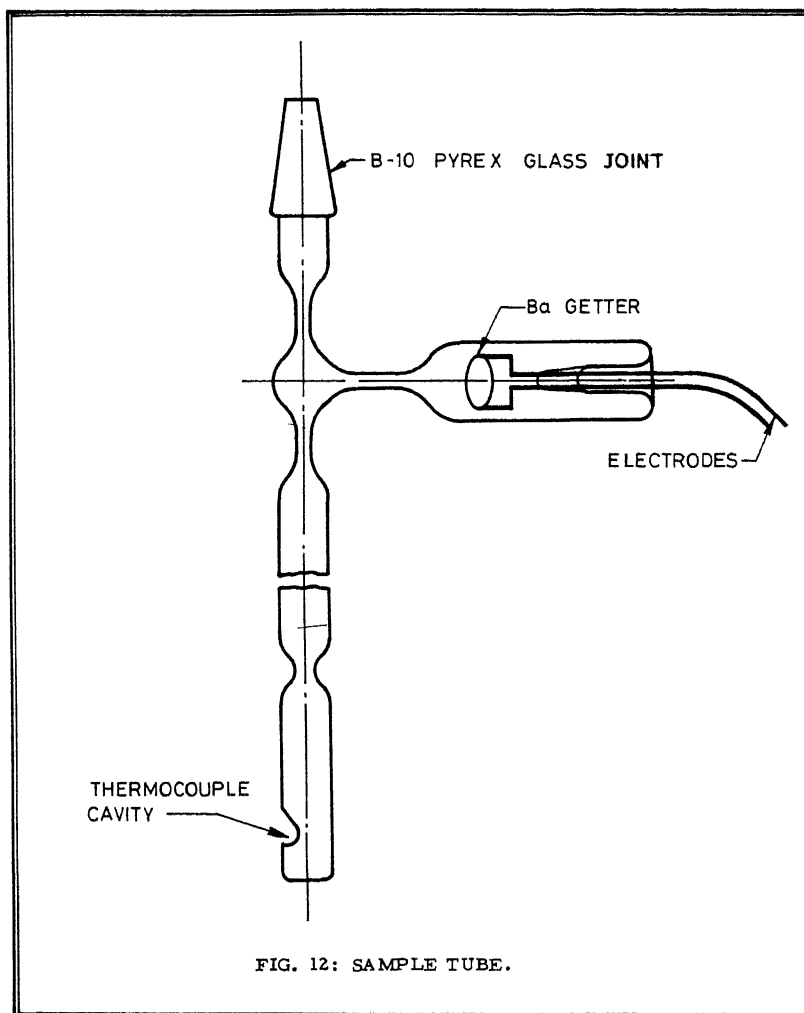
^{*}Obtained through the curtesy of Prof. M. Satyam of the Indian Institute of Science, Bangalore and Bharat Electronic Ltd., Bangalore, India.

^{**}

The chemicals thiophene and 1,2-dichloroethane were kindly provided by Professors C.N.R. Rao and M.V. George respectively both from the Department of Chemistry, I.I.T. Kanpur.

^{***}

We thank Dr. D. Devaprabhakara and Miss Indu Mehrotra, Department of Chemistry, I.I.T. Kanpur for help in distilling the samples.



III.G Photographs of the Spectrometer

A photograph of the spin-echo spectrometer console is shown in Fig. 13. Figure 14 shows a photograph of the magnet and cryostat assembly.

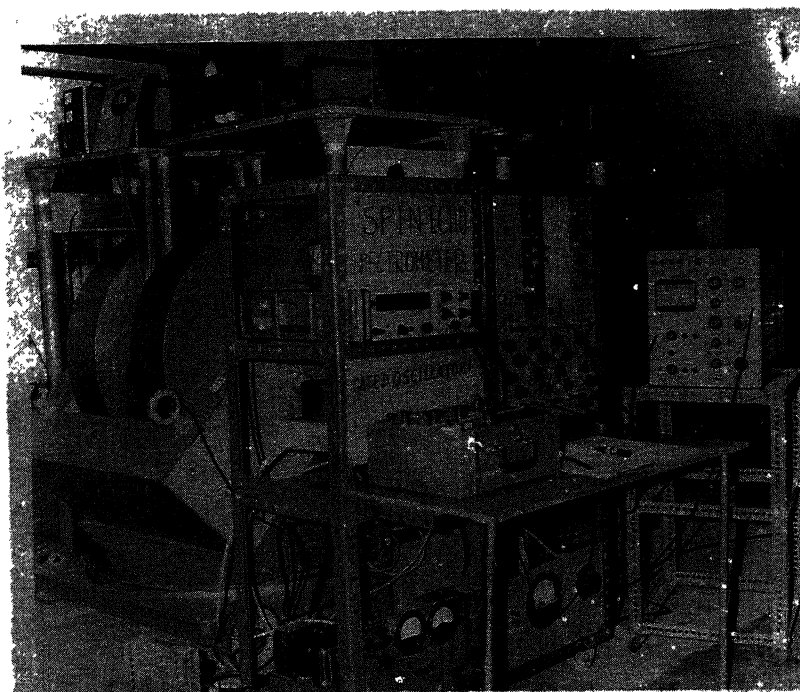


FIG. 13: SPIN-ECHO SPECTROMETER CONSOLE.

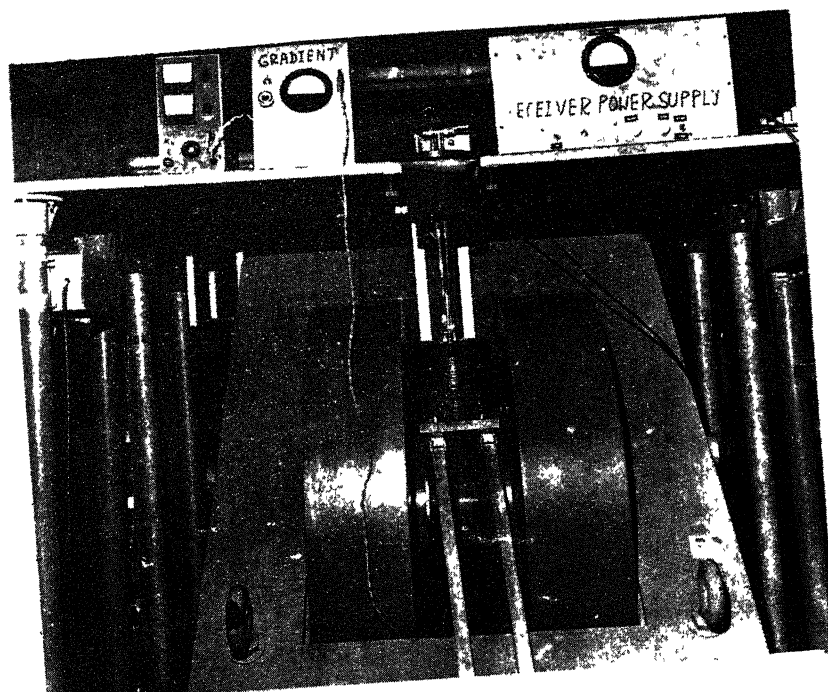


FIG. 14: MAGNET AND CRYOSTAT ASSEMBLY.

Chapter IV

PROTON SPIN RELAXATION AND MOLECULAR MOTION IN THIOPHENE AND FURAN

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PROTON SPIN RELAXATION AND MOLECULAR MOTION IN THIOPHENE^{*} AND FURAN^{**}

IV.A Introduction

In this chapter a study of proton spin-lattice relaxation and molecular motion in the liquids thiophene and furan is presented. The results on T_1 and D in thiophene are shown in Figs. 15 and 16 respectively. T_1 varies from 24.0 sec at 300°K to 72.0 sec at 550°K with a maximum of 94.0 sec at 490°K. D varies from 2.4×10^{-5} cm²/sec at 300°K to 38.0×10^{-5} cm²/sec at 550°K. For furan (see Fig. 17) T_1 varies from 39.0 sec at 295°K to 66.0 sec at 405°K with a maximum of 95.0 sec at 373°K and D varies monotonically from 5.5×10^{-5} cm²/sec to 36.0×10^{-5} cm²/sec in the same temperature range. The contribution of the intermolecular dipolar interaction is separated from the observed relaxation rates on the basis of a translational diffusion theory (see Sec. II.C) using the D values measured. The remaining contribution is analysed in terms of the intramolecular dipolar interactions and the spin-rotation interactions using the theory of anisotropic rotational diffusion (see Sec. II.C) to obtain the rotational diffusion constants of the molecule and the correlation times for reorientation and angular velocity changes and their temperature dependences. An estimate of the spin-rotation interaction constant of protons is made for both the molecules.

* The work on thiophene molecule in this chapter would be published in J. Chem. Phys. 55 (1971) 51.

** The work on furan is to be published in J. Chem. Phys. (1972)

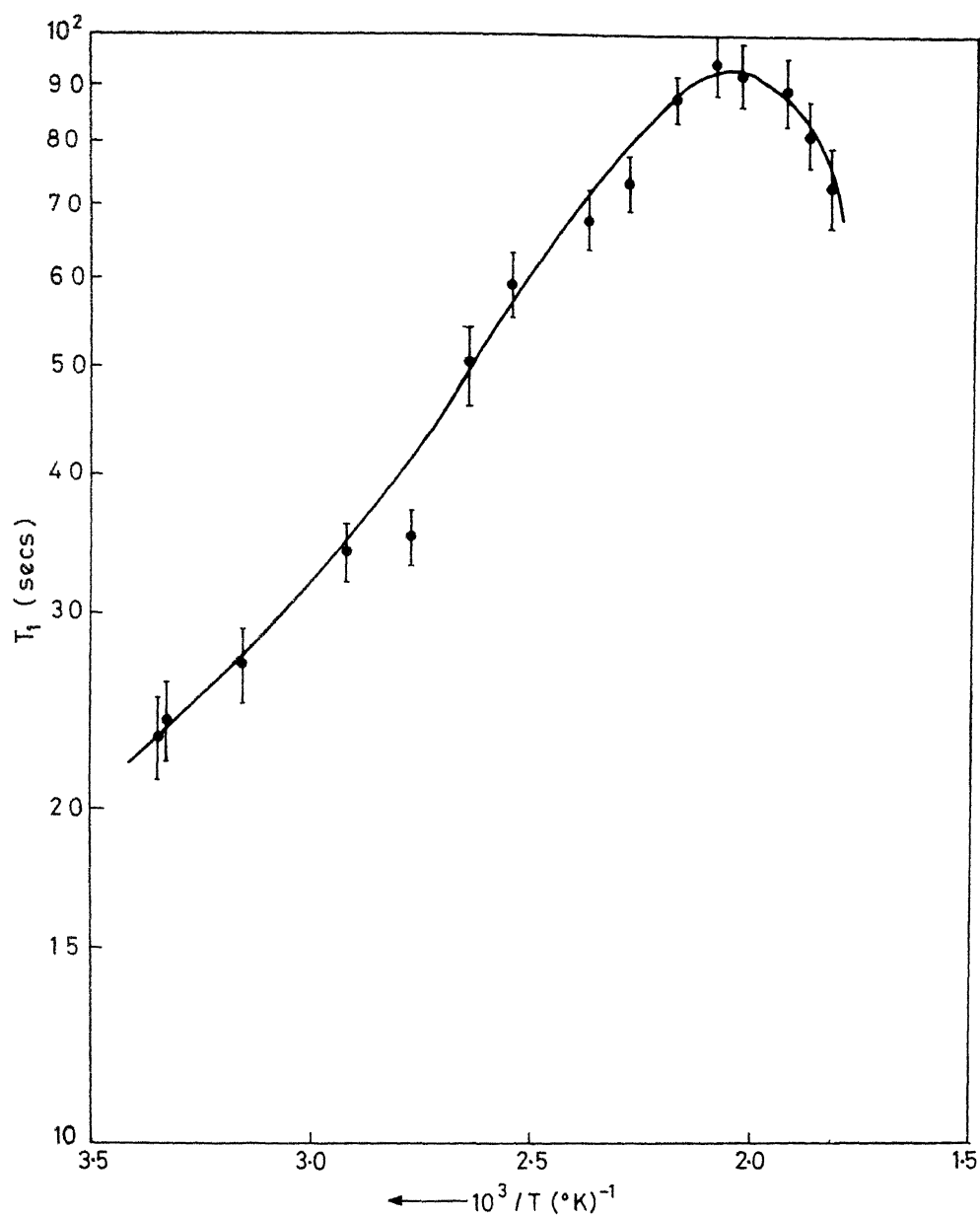


FIG. 15: TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME, T_1 , IN THIOPHENE.

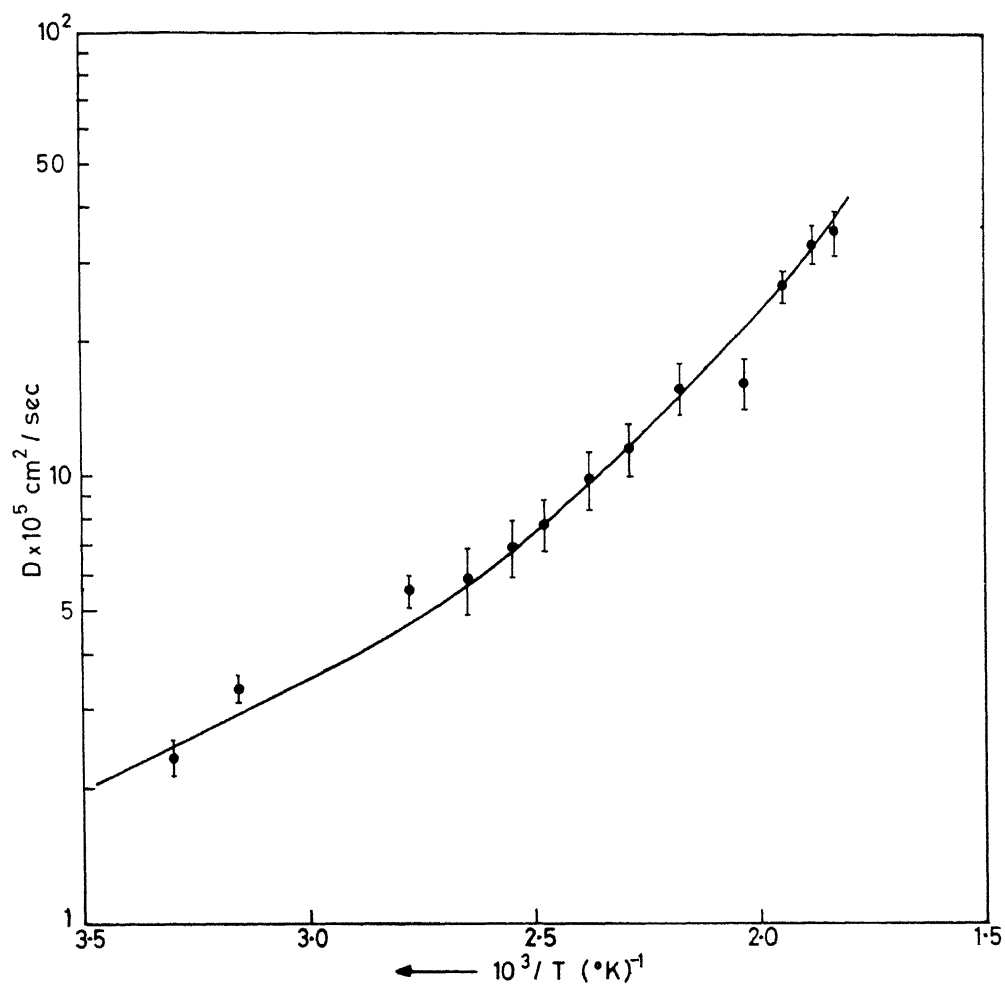


FIG. 16: TEMPERATURE DEPENDENCE OF COEFFICIENT OF SELF-DIFFUSION, D , OF THIOPHENE.

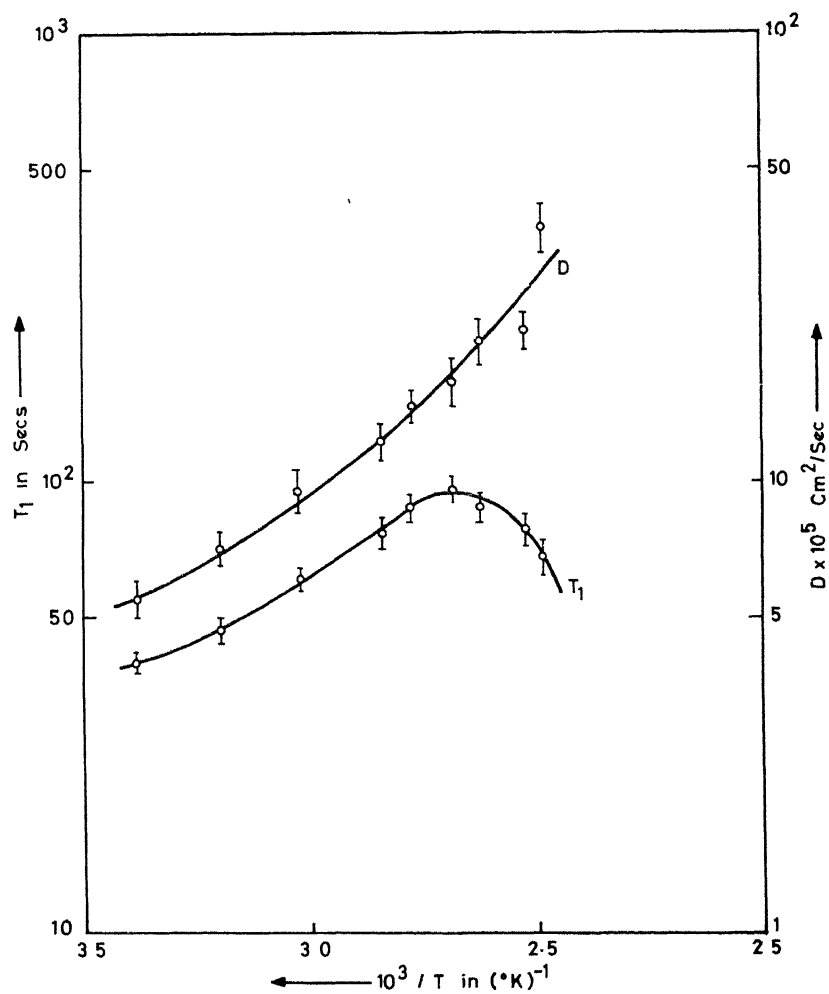


FIG. 17. TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME, T_1 , AND COEFFICIENT OF SELF-DIFFUSION, D , IN FURAN.

The geometrical arrangement^{68,69} of the four protons in these molecules (see Fig. 18) introduces an additional feature into the analysis of the present experimental data which may be of importance in other molecules as well. This arises due to the fact that the two protons close to the sulphur (thiophene) and oxygen (furan) experience much weaker intramolecular dipolar interactions compared to the other two protons. It can be shown on the basis of Sec.II.D that the approach to equilibrium of the z-component of total magnetization is governed by a superposition of two exponentials. The decays observed in the present case, however, showed a single exponential (see Fig. 19) since, as the analysis showed, the exponential with the longer time constant never has an amplitude greater than one-tenth of the other.

IV.B Relaxation Rates in Thiophene and Furan

The only magnetic nuclei in these molecules are the four protons (apart from the 1% natural abundance of C^{13}). The occurrence of the maxima in the T_1 vs $10^3/T$ graphs (Figs. 15 and 17) shows that the spin-rotation interaction of protons is operative as a mechanism of relaxation in addition to the inter- and intra-molecular dipolar interactions.

An important distinction appears between the relaxation rates of the two protons labelled I_1 , I_2 and those labelled S_1 , S_2 . For example, in thiophene S_1 and S_2 are 2.64 \AA apart and are at the same distance (2.64 \AA) from I_1 and I_2 respectively. I_1 and I_2 are 4.54 \AA apart. The distances are approximately the

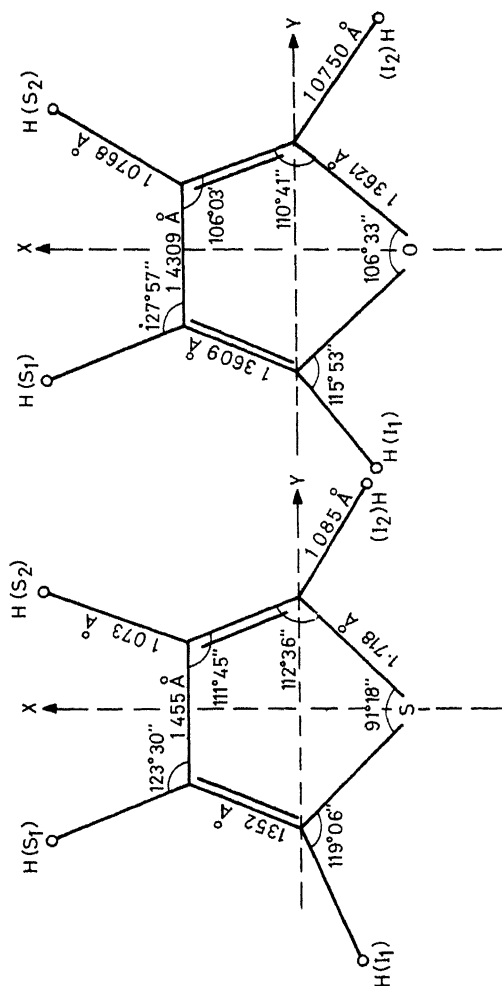


FIG. 18: MOLECULAR STRUCTURE OF THIOPHENE AND FURAN.

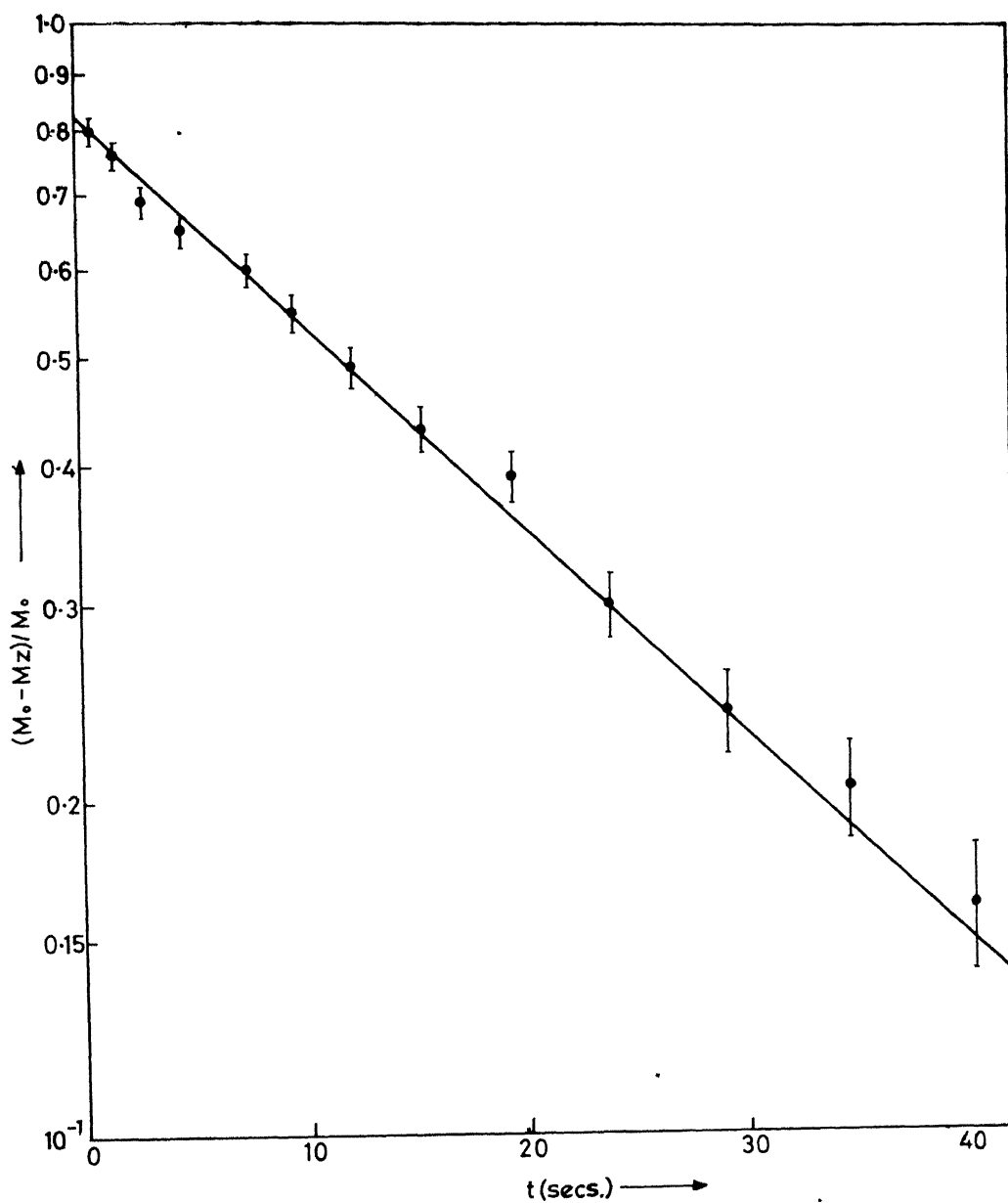


FIG. 19: A TYPICAL T_1 -DECAY IN THIOPHENE USING A $\pi/2 - t - \pi/2 - \tau - \pi$
- τ - ECHO SEQUENCE.

same in furan. Since the relaxation rate arising from the dipolar interaction is proportional to the inverse sixth power of the internuclear distance the dipolar interaction between $(I_1; I_2)$, $(I_1; S_2)$ and $(I_2; S_1)$ are negligible compared to the other three $(I_1; S_1)$, $(S_1; S_2)$ and $(I_2; S_2)$. The protons I_1 and I_2 , therefore, experience much weaker intramolecular dipolar interactions compared to S_1 and S_2 .

For the purpose of writing the rate equations it is convenient to define

$$\underline{I} = \underline{I}_1 + \underline{I}_2$$

and

$$(IV.1)$$

$$\underline{S} = \underline{S}_1 + \underline{S}_2 .$$

The equations of motion for $\langle I_z \rangle$ and $\langle S_z \rangle$ can be obtained, by using Eqs. (II.38), (II.63) to (II.68) and adding the spin-rotation interaction, to be

$$-\frac{d}{dt} \langle I_z \rangle = k_I (\langle I_z \rangle - I_0) + \frac{k_C}{2} [2(\langle I_z \rangle - I_0) + (\langle S_z \rangle - S_0)],$$

(IV.2)

$$-\frac{d}{dt} \langle S_z \rangle = k_S (\langle S_z \rangle - S_0) + \frac{k_C}{2} [2(\langle S_z \rangle - S_0) + (\langle I_z \rangle - I_0)],$$

with the rate constants k_I , k_S and k_C given by

$$k_I = (T_1^{SR})^{-1} + (2T_1^{inter})^{-1} \quad (IV.3)$$

$$k_S = (T_1^{SR})^{-1} + (2T_1^{inter})^{-1} + \frac{3}{2} \gamma^4 \hbar^2 r_S^{-6} \tau_S ,$$

(IV.4)

$$k_C = (3T_1^{inter})^{-1} + \gamma^4 \hbar^2 r_{IS}^{-6} \tau_{IS} , \quad (IV.5)$$

where r_S is the distance between S_1 and S_2 ; r_{IS} that between I_1 and S_1 (or I_2 and S_2); τ_S and τ_{IS} are the correlation times appropriate for the dipolar interactions $(S_1; S_2)$ and $(I_1; S_1)$ (or $(I_2; S_2)$) respectively. $(T_1^{SR})^{-1}$ and $(T_1^{inter})^{-1}$ are the relaxation rates if the spin-rotation interaction and the inter-molecular dipolar interactions respectively were responsible for relaxation. Equations (IV.2) are identical to those given by Brooks et al.⁵⁰ for the relaxation of two different groups of nuclei on a molecule. In the present case the rate constants are explicitly identified in Eqs. (IV.3) to (IV.5). These authors have shown that the solution of Eqs. (IV.2) representing the growth of the total magnetization $M_Z = \langle I_Z + S_Z \rangle$ following a $\pi/2$ -pulse to equilibrium value M_O is, in general, a sum of two exponentials given by

$$\frac{M_O - M_Z}{M_O} = a_+ \exp(-k_+ t) + a_- \exp(-k_- t), \quad (IV.6)$$

with

$$k_{\pm} = \frac{1}{2}(k_I + k_S + 2k_C \pm R), \quad (IV.7)$$

$$a_{\pm} = \frac{1}{2}\left(1 \mp \frac{k_C}{R}\right), \quad (IV.8)$$

$$R = +[(k_I - k_S)^2 + k_C^2]^{\frac{1}{2}}, \quad (IV.9)$$

The relaxation decays observed in thiophene and furan, however, do not reveal two exponentials since a_- always has a value < 0.1 . The relaxation rate observed is then given by

$$\begin{aligned}
k_{\text{obs}} = (T_1)_{\text{obs}}^{-1} &= [5(6T_1^{\text{inter}})^{-1}] + [(T_1^{\text{SR}})^{-1}] + [\gamma^4 h^2 (\frac{3}{4} \tau_S r_S^{-6} \\
&\quad + \tau_{\text{IS}} r_{\text{IS}}^{-6}) \\
&\quad + \frac{1}{2} (\{\frac{3}{2} \gamma^4 h^2 \tau_S r_S^{-6}\}^2 + \{(3T_1^{\text{inter}})^{-1} \\
&\quad + \gamma^4 h^2 \tau_{\text{IS}} r_{\text{IS}}^{-6}\}^2)^{\frac{1}{2}}] . \tag{IV.10}
\end{aligned}$$

It must be noted that k_{obs} is not a linear superposition of the contributions of the type $(T_1^{\text{inter}})^{-1} + (T_1^{\text{intra}})^{-1} + (T_1^{\text{SR}})^{-1}$ as one would be tempted to write if the cross-relaxation effects are not examined.

IV.C Analysis

For the purpose of analysing the experimental results we shall define the observed relaxation rate as

$$(T_1)_{\text{obs}}^{-1} = k_{\text{obs}} = k_{\text{inter}} + k_{\text{intra}} , \tag{IV.11}$$

where

$$k_{\text{intra}} = k_{\text{SR}} + k_{\text{DD}} , \tag{IV.12}$$

with

$$k_{\text{inter}} = 5(6T_1^{\text{inter}})^{-1} , \tag{IV.13}$$

$$k_{\text{SR}} = (T_1^{\text{SR}})^{-1} , \tag{IV.14}$$

and

$$\begin{aligned}
k_{\text{DD}} &= \gamma^4 h^2 \left[\frac{3}{4} \tau_S r_S^{-6} + \tau_{\text{IS}} r_{\text{IS}}^{-6} \right] + \frac{1}{2} \left[\left\{ \frac{3}{2} \gamma^4 h^2 r_S^{-6} \tau_S \right\}^2 \right. \\
&\quad \left. + \{(3T_1^{\text{inter}})^{-1} + \gamma^4 h^2 \tau_{\text{IS}} r_{\text{IS}}^{-6}\}^2 \right]^{\frac{1}{2}} . \tag{IV.15}
\end{aligned}$$

The division of relaxation rates in Eqs. (IV.11) and (IV.12) is merely for convenience and the subscripts are somewhat arbitrary since k_{inter} does not include all the contribution from intermolecular dipolar interactions and k_{DD} contains some cross-relaxation terms arising from the same.

1. Intermolecular dipolar interactions: Using the results of Sec. II.C we have, in the 'hard-sphere' limit, the intermolecular relaxation rate as

$$(T_1^{\text{inter}})^{-1} = \frac{4\pi}{5} \frac{\gamma^4 \hbar^2}{Ma} \left(\frac{\rho}{D}\right) . \quad (\text{IV.16})$$

In the above expression ρ values have been calculated using room temperature densities and temperature coefficients for thiophene available in literature⁷⁰. Viscosity data⁷⁰ on thiophene between 20°C and 80°C used along with D values gave a value of $1.54 \pm 0.05 \text{ \AA}$ for 'a'. Since the data is not available for furan the same value of 'a' has been used. Substituting the relevant constants one gets

$$\begin{aligned} k_{\text{inter}}(\text{thiophene}) &= 5.506 \times 10^{-7} \left(\frac{\rho}{D}\right) , \\ k_{\text{inter}}(\text{furan}) &= 6.808 \times 10^{-7} \left(\frac{\rho}{D}\right) . \end{aligned} \quad (\text{IV.17})$$

The values of k_{obs} , k_{inter} along with the resulting k_{intra} for thiophene and furan are plotted in Figs. 20 and 21 respectively.

2. Intramolecular dipolar interactions and spin-rotation interactions:

The analysis of k_{intra} is carried out on the basis of the theory of anisotropic rotational diffusion discussed

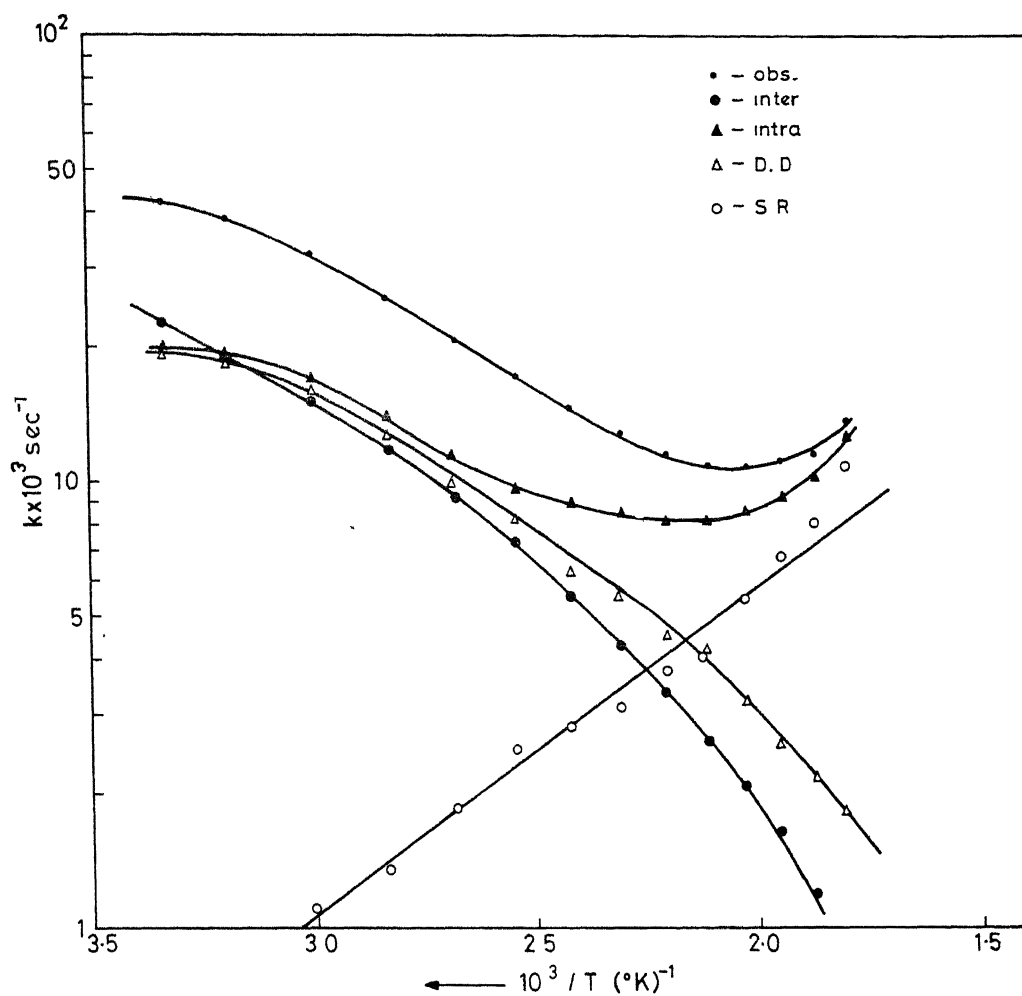


FIG. 20: PLOTS OF THE VARIOUS RELAXATION RATES IN THIOPHENE AS FUNCTIONS OF TEMPERATURE. THE VARIOUS k 's ARE DEFINED IN EQS. (IV. 11) to (IV. 15).

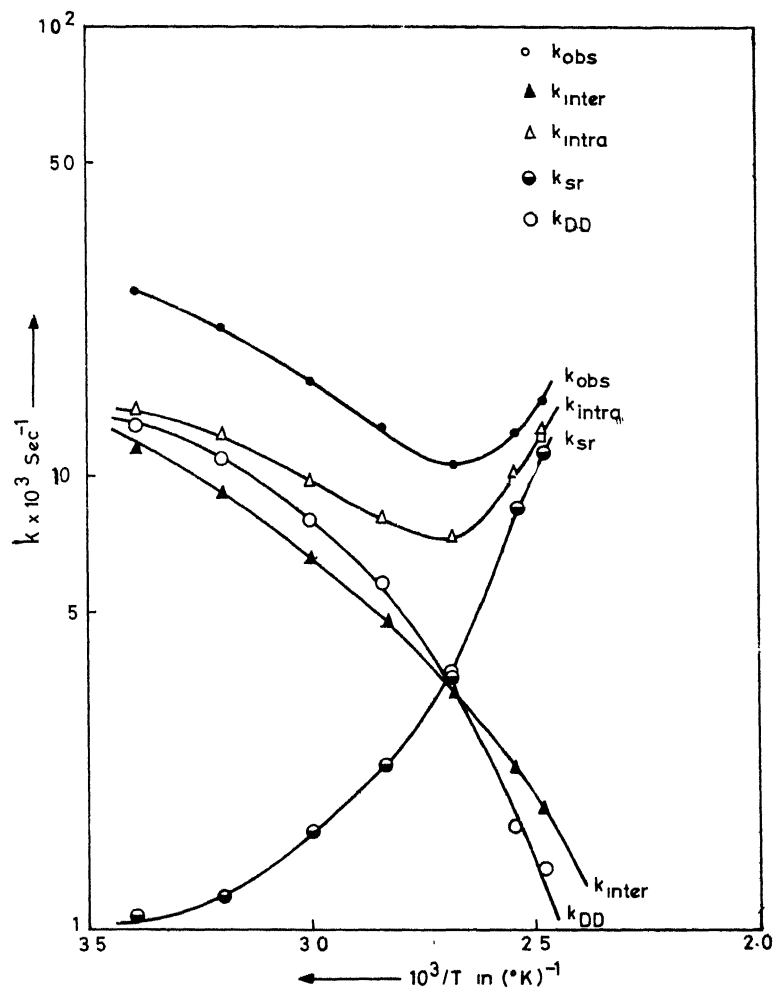


FIG. 21: PLOTS OF THE VARIOUS RELAXATION RATES IN FURAN AS FUNCTIONS OF TEMPERATURE. THE VARIOUS k 's ARE DEFINED IN EQS. (IV.11) TO (IV.15).

in Sec. II.C. Since both these molecules are planar and have an additional plane of symmetry the principal axis of the diffusion tensor and the moment of inertia tensor coincide¹⁵ (see X and Y marked in Fig. 18). The third axis is perpendicular to the plane of the molecule. Using Eq. (II.48) and the structural data of the molecules the correlation times τ_S and τ_{IS} can be calculated. k_{SR} is given by Eq. (II.58). Since there is no information regarding the spin-rotation interaction tensor for different protons it will be assumed that this mechanism contributes equally to each of them. The values of C_{ii} or C_t are not known for these molecules. Further analysis of the data on the basis of Eqs. (II.48) and (II.58), as they are given, is difficult because of too many unknown quantities. In order to proceed with the analysis we assume that τ_J is isotropic i.e. it is the same for the three principal axes. This relates the three diffusion constants ^{the} in ratios of the corresponding moments of inertia. There is no a priori justification for this assumption.* If the analysis on this basis yields reasonable values for the diffusion constants and their variation with temperature the approximation would be acceptable. Under this approximation Eq. (II.58) becomes

* This approximation implies that the molecular collisions affect the reorientation about the three axes with equal efficiency. From Eqs. (II.60) and (II.61) it can be seen that this approximation also implies that the ensemble average of the second derivative of the intermolecular potential is isotropic^{15,41}.

$$k_{SR} = C'D_{\perp} \quad (\text{IV.18})$$

where

$$C' = \frac{2}{3} I_{\perp} \sum_{i=x,y,z} [C_{ii}^2 - 2C_t(C_{ii} - C_t)] I_i, \quad (\text{IV.19})$$

which is a constant for the molecule. Substituting $\varphi_S = 90^\circ$ and $\varphi_{IS} = 111^\circ 3'$ and I_x, I_y, I_z as 62.8568, 93.2944 and 156.2164 amu \AA^2 respectively for thiophene⁶⁸ one gets

$$\tau_S = \frac{0.1007}{D_{\perp}} \quad \text{and} \quad \tau_{IS} = \frac{0.1206}{D_{\perp}}. \quad (\text{IV.20})$$

For furan⁶⁹ φ_S and φ_{IS} are 90° and $165^\circ 51'$ and I_x, I_y and I_z are respectively 54.6720, 53.5126 and 108.2304 amu \AA^2 so that

$$\tau_S = \frac{0.1153}{D_{\perp}} \quad \text{and} \quad \tau_{IS} = \frac{0.1140}{D_{\perp}}. \quad (\text{IV.21})$$

Further, r_S and r_{IS} are 2.64 \AA for thiophene and are 2.756 \AA and 2.735 \AA respectively for furan. We have then

$$\begin{aligned} (k_{DD})_{\text{thiophene}} &= \frac{3.301 \times 10^8}{D_{\perp}} + \frac{1.015 \times 10^8}{D_{\perp}} \\ &\quad \times [1.586 + (1 + 1.086 \times 10^{-15} \frac{\rho}{D} D_{\perp})^2]^{\frac{1}{2}} \\ (k_{DD})_{\text{furan}} &= \frac{2.6763 \times 10^8}{D_{\perp}} + \frac{0.776 \times 10^8}{D_{\perp}} \\ &\quad \times [2.107 + (1 + 1.756 \times 10^{-15} \frac{\rho}{D} D_{\perp})^2]^{\frac{1}{2}}. \end{aligned} \quad (\text{IV.22})$$

The condition for a minimum in k_{intra} can now be considered in terms of Eqs. (IV.18) and (IV.22) by treating the quantity under the radical in Eq. (IV.22) as constant with respect to temperature since the contribution of $\frac{\rho D_{\perp}}{D}$ is small and does not vary as rapidly as D_{\perp} . This gives

Mol.	T _{min}	D _⊥ (T _{min})x10 ⁻¹¹ sec ⁻¹	τ _J (T _{min})x10 ¹⁴ sec	C'x10 ¹⁴
Thiophene	462°K	1.30	5.2	3.160
Furan	373°K	1.28	4.5	2.852

The values of D_⊥ and τ_J are reasonable. To see the implication of C' we shall equate it to $(\frac{2}{3} C_t^2 I_{\perp} \sum_i I_i)$ its value if just the scalar part of the spin-rotation interaction is considered.

This gives

$$C_t = \frac{1}{3} \sum_i C_{ii} \leq 1.00 \text{ kHz (for thiophene)} \quad (\text{IV.23})$$

$$\leq 1.40 \text{ kHz (for furan),}$$

Powles and Figgins⁴³ estimate C_t = 3.8 kHz for benzene from relaxation measurements. Ramsey⁴⁵ estimates C_t < 1.0 kHz for benzene from molecular beam data. In view of this the values of C_t given in Eq. (IV.23) seem reasonable.

Substituting for C' in the expressions for k_{intra} and using Eq.(IV.17) allows the determination of D_⊥ at any temperature. The values of D_⊥ along with the corresponding τ_J's for thiophene and furan are plotted in Figs. 22 and 23 respectively. It may be noted that the condition τ_J << τ_S, τ_{IS} required for writing Eq. (II.58) is satisfied. Figures 20 and 21 also show k_{SR} and k_{DD} as functions of temperature for the two cases.

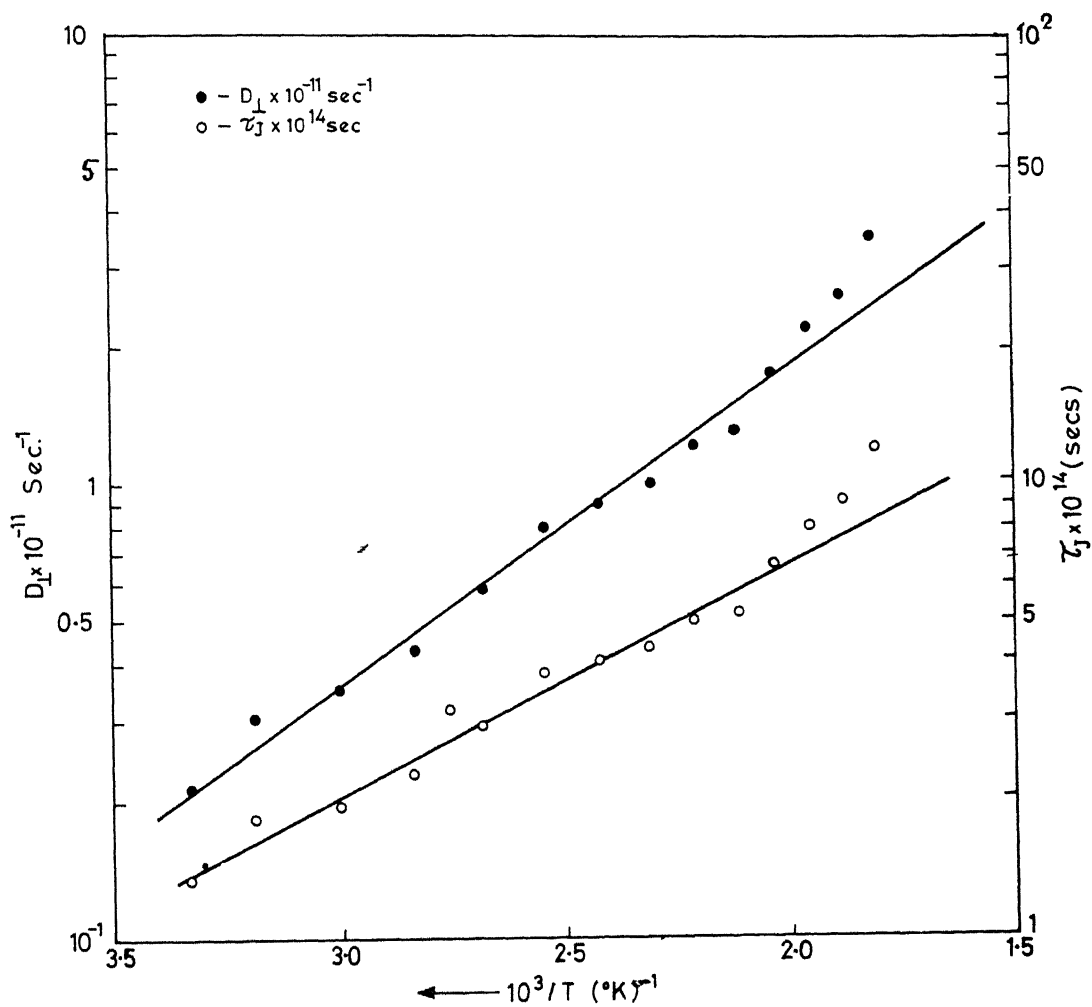


FIG. 22: TEMPERATURE DEPENDENCE OF D_{\perp} AND τ_J FOR THIOPHENE.

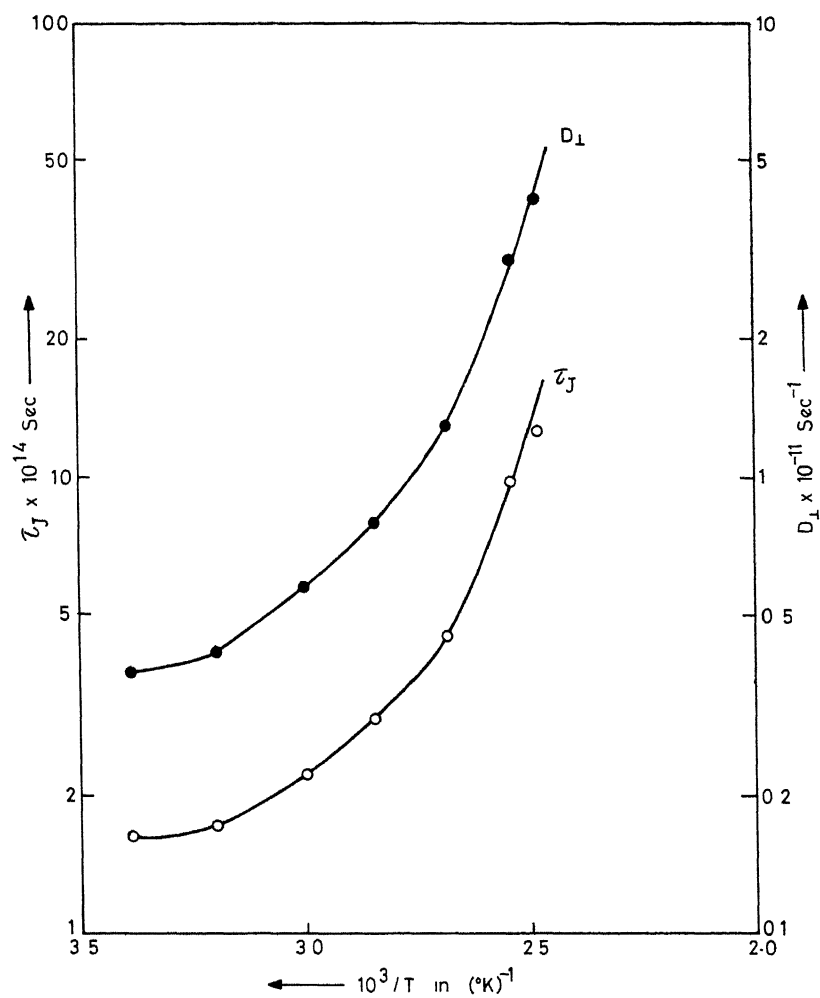


FIG. 23: TEMPERATURE DEPENDENCE OF D_L AND τ_J FOR FURAN.

IV.D Discussion

Figure 22 shows that upto 500°K in thiophene D_{\perp} obeys an Arrhenius equation:

$$D_{\perp}(T) = D_{\perp}(0) \exp \left[- E_{D_{\perp}}/RT \right], \quad (\text{IV.24})$$

where $D_{\perp}(T)$ is the value of D_{\perp} at $T^{\circ}\text{K}$, $E_{D_{\perp}}$ is the activation energy and R is the gas constant. The deviation at higher temperatures is probably due to the fact that the reorientational motion in the liquid is not completely diffusional and inertial effects come into play. The activation energy obtained from the plot is 3.2 kcal/mole. In the case of furan (see Fig. 23) D_{\perp} does not have an Arrhenius character at all.

For thiophene the value of χ_{\perp} (see Eq. (II.62)) at 300°K is about 7.0. It drops to about 2.0 at 480°K and is about 0.8 at 500°K. The motion of thiophene molecules about an axis perpendicular to the molecular plane can be considered diffusional upto about 480°K. For furan χ_{\perp} varies from 10.9 at 292°K to 1.1 at 403°K so that one might expect the motion to be diffusional upto 380°K.

A computation of the amplitudes a_{\pm} of the two exponentials in Eq. (IV.6) with the parameters determined by the analysis shows that the largest value of a_{-} over the temperature range considered in both the cases is less than 0.1. The longer time constant would, therefore, not be observable with the precision of our experiments.

The determination of the contribution of the three mechanisms and the parameters thereof rests on two approximations (a) the contribution of the intermolecular interaction is given by a 'hard-sphere' model translational diffusion theory and (b) the angular velocity correlation time τ_J is isotropic. The error introduced by (a) may not be serious since this approximation has been found to be valid for other liquids^{26,43}. The second approximation was made to reduce the number of independent parameters entering the theory of rotational diffusion. The results obtained on D_{\perp} and τ_J indicate that it is satisfactory.

Chapter V

PROTON SPIN RELAXATION IN MONOBROMOTHIOPHENES

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PROTON SPIN RELAXATION IN MONOBROMOTHIOPHENES*

In this chapter the experimental results on proton spin-lattice relaxation times in 2- and 3-bromothiophenes in the temperature range 300°K to 450°K and their analysis is presented. The experimental results for T_1 and D for 2- and 3-bromothiophenes are shown in Figs. 24 and 25 respectively.

V.A Analysis and Discussion

The analysis of the relaxation data for both these molecules has been performed in terms of two significant mechanisms, namely, the inter- and intramolecular dipolar interactions. Spin-rotation interaction is expected to contribute very little in the temperature range studied. Measurements were not made at temperatures higher than 450°K due to incipient decomposition.

The molecular structures of 2- and 3-bromothiophenes are shown in Fig. 26. Assuming that the interproton distances in these molecules are approximately the same as those in thiophene⁵¹ it can be seen that in 2-bromothiophene only the dipolar interactions ($I_1;S$) and ($I_2;S$) are significant while in 3-bromothiophene only ($S_1;S_2$) is significant. There are, in principle, two correlation times entering the calculation for 2-bromothiophene but for the present analysis these are set

*The work in this chapter would appear in J. Chem. Phys. 57 (1972)71

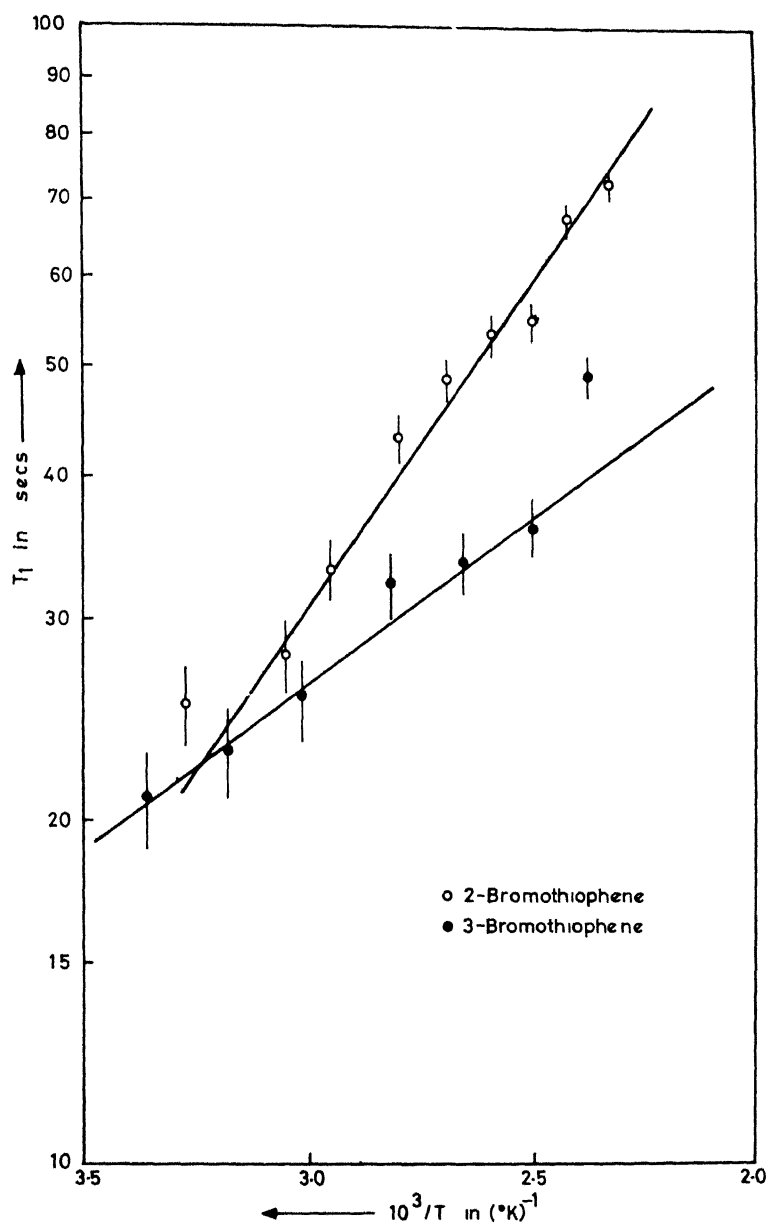


FIG. 24: SPIN-LATTICE RELAXATION TIME, T_1 , AS A FUNCTION OF TEMPERATURE IN 2- AND 3- BROMOTHIOPHENES.

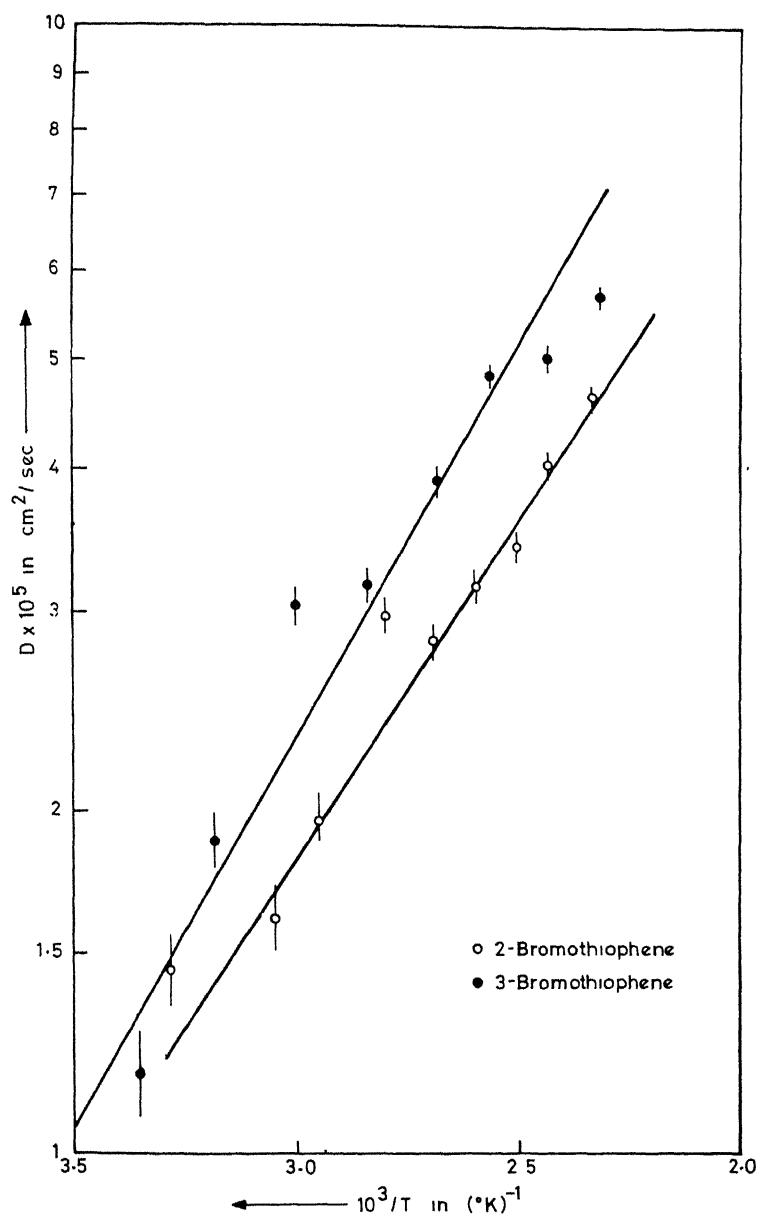


FIG. 25: COEFFICIENT OF SELF-DIFFUSION, D , AS A FUNCTION OF TEMPERATURE IN 2- AND 3-BROMOTHIOPHENES.

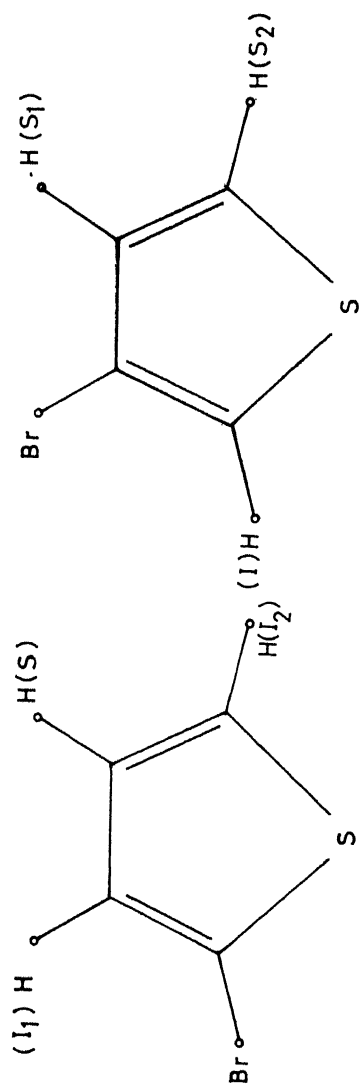


FIG. 26: MOLECULAR STRUCTURE OF 2-AND 3-BROMOTHIOPHENES.

equal to each other. In both these molecules two of the three protons experience intramolecular dipolar interactions of the same strength, which is different from that felt by the third proton. Invoking this fact and using the standard theoretical procedures described in Secs. II.C and II.D, it can be shown that the equations of motion for $\langle I_z \rangle$ and $\langle S_z \rangle$ are given by⁵⁰

$$-\frac{d}{dt} \langle I_z \rangle = k_I (\langle I_z \rangle - I_0) + k_C [2f_S (\langle I_z \rangle - I_0) + f_I (\langle S_z \rangle - S_0)] ,$$

(V.1)

and

$$-\frac{d}{dt} \langle S_z \rangle = k_S (\langle S_z \rangle - S_0) + k_C [2f_I (\langle S_z \rangle - S_0) + f_S (\langle I_z \rangle - I_0)] ,$$

where $\langle I_z \rangle$ and $\langle S_z \rangle$ are the magnetizations and f_I and f_S are the fractions of the total number of spins of type I and S (indicated in Fig. 26) respectively. The rate constants k_I , k_S and k_C for the two molecules are

	2-bromothiophene	3-bromothiophene
k_I	$2(3T_1^{\text{inter}})^{-1}$	$(3T_1^{\text{inter}})^{-1}$
k_S	$(3T_1^{\text{inter}})^{-1}$	$2(3T_1^{\text{inter}})^{-1} + \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_r$
k_C	$(3T_1^{\text{inter}})^{-1} + \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_r$	$(3T_1^{\text{inter}})^{-1}$

where r is the distance between any two adjacent protons (set equal to the corresponding value in thiophene), τ_r is the rotational correlation time and $(T_1^{\text{inter}})^{-1}$ refers to the relaxation rate if the intermolecular interactions were the only mechanisms for relaxation. The solution of Eq. (V.1) for

the growth of the net magnetization $M_Z = \langle I_Z + S_Z \rangle$ following a $\pi/2$ -pulse is a sum of two exponentials

$$\frac{M_O - M_Z}{M_O} = a_+ \exp(-k_+ t) + a_- \exp(-k_- t), \quad (V.3)$$

where $M_O = (I_O + S_O)$ and

$$k_{\pm} = \frac{1}{2}(k_I + k_S + 2k_C \pm R), \quad (V.4)$$

with

$$a_{\pm} = \frac{1}{2} \left[1 \mp \frac{(k_I - k_S)(f_S - f_I) + 3k_C(f_S - f_I)^2 - k_C}{R} \right], \quad (V.5)$$

and

$$R = \left[\{(k_I - k_S) + 2k_C(f_S - f_I)\}^2 + 4f_S f_I k_C^2 \right]^{1/2}. \quad (V.6)$$

The experimentally observed T_1 -decays in both the cases, however, consist of single exponentials since, as the final analysis showed, the longer time constant is either too long or has too small an amplitude to be observed. The observed relaxation rate is, therefore, given by

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{\text{obs}} = & 5(6T_1^{\text{inter}})^{-1} + \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_r + \left[(6T_1^{\text{inter}})^{-2} + \frac{3}{4} \left(\frac{\gamma^4 \hbar^2}{r^6} \tau_r \right)^2 \right. \\ & \left. + \frac{\gamma^4 \hbar^2}{r^6} \tau_r (6T_1^{\text{inter}})^{-1} \right]^{1/2}, \end{aligned} \quad (V.7)$$

for 2-bromothiophene and

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{\text{obs}} = & 5(6T_1^{\text{inter}})^{-1} + \frac{3}{4} \frac{\gamma^4 \hbar^2}{r^6} \tau_r + \left[(6T_1^{\text{inter}})^{-2} + \left(\frac{3}{4} \frac{\gamma^4 \hbar^2}{r^6} \tau_r \right)^2 \right. \\ & \left. + \frac{\gamma^4 \hbar^2}{r^6} \tau_r (12T_1^{\text{inter}})^{-1} \right]^{1/2}, \end{aligned} \quad (V.8)$$

for 3-bromothiophene.

Rotational correlation times for the two molecules can be obtained if, $(T_1^{\text{inter}})^{-1}$, given by

$$(T_1^{\text{inter}})^{-1} = \frac{3\pi}{5} \frac{\gamma_h^4 + 2}{Ma} \left(\frac{\rho}{D}\right), \quad (\text{V.9})$$

can be estimated at all temperatures. The D values used are obtained experimentally over the desired temperature range. A value of 'a' compatible with D and the coefficient of viscosity ' η ' over this temperature range could not be determined since data on ' η ' is not available. It is, therefore, assumed that 'a' has the same value as for thiophene viz. 1.54 \AA for both the molecules. This gives

$$(T_1^{\text{inter}})^{-1} = 2.552 \times 10^{-7} \left(\frac{\rho}{D}\right). \quad (\text{V.10})$$

Density values at different temperatures were estimated using known densities at 20°C and the temperature coefficients for thiophene.

Eliminating $(T_1^{\text{inter}})^{-1}$ estimated as above from the observed relaxation rates the rotational correlation times for both the molecules are determined over the temperature range studied. These are shown in Fig. 27. The two curves are in sharp contrast considering the fact that the molecules are somewhat similar. It can be seen that the variation of τ_r with temperature for 2-bromothiophene is similar to what is normally expected. The activation energy for this variation is

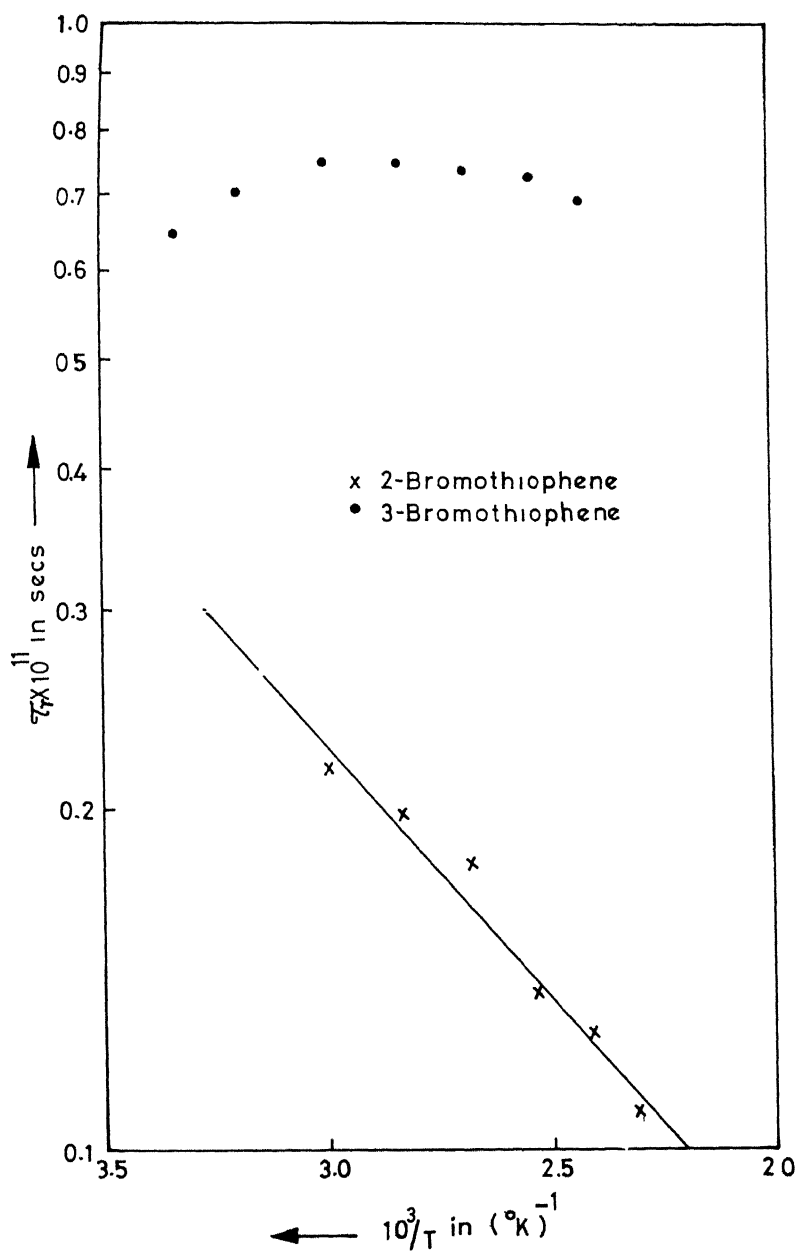


FIG. 27: VARIATION OF τ_r WITH TEMPERATURE IN 2- AND 3- BROMO THIOPHENES.

2.0 kcal/mole. For 3-bromothiophene, however, τ_r remains essentially unchanged with temperature indicating a large value for the activation energy. It must be noted that the values given in Fig. 27 are not very accurate since several assumptions were made regarding the structural and motional constants due to lack of data. However, the contrast in the trend of variation of τ_r , even after allowing for the errors in the above estimates, is unmistakable.

Chapter VI

PROTON SPIN RELAXATION IN LIQUID 1,2-DICHLOROETHANE

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PROTON SPIN-RELAXATION IN LIQUID 1,2-DICHLOROETHANE

VI.A Introduction

This chapter presents a study on proton spin-lattice relaxation in 1,2-dichloroethane. T_1 and D have been measured in the temperature range 300°K to 430°K . The results are shown in Fig. 28. The analysis of the results on this system shows that the relaxation behavior and the motional characteristics of this molecule are somewhat different from what one might expect from the results on the systems described in Chapter IV and V. We are here, however, dealing with a molecule of different shape. The possibility of scalar coupling with chlorine nuclei and dipolar interactions modulated by rotamer exchange contributing to relaxation have been examined and found to be negligible. The observed relaxation rates have been analysed in terms of inter- and intramolecular dipolar ~~interactions~~ using the results of Chapter II and it is seen that the rotational correlation time τ_r is essentially independent of temperature. It is suspected that the motion may not be diffusional and the possibility of inertial effects governing the molecular motion has been investigated.

VI.B Analysis

An inspection of the molecule shows that the various mechanisms which might contribute to relaxation are the scalar

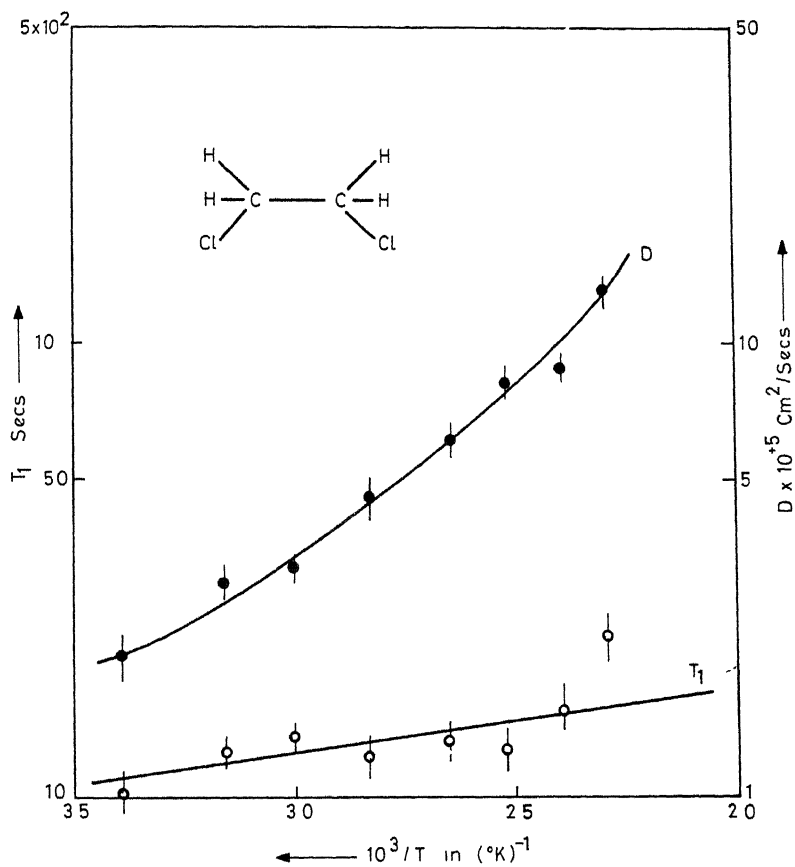


FIG. 28: TEMPERATURE DEPENDENCE OF PROTON SPIN-LATTICE RELAXATION TIME, T_1 , AND COEFFICIENT OF SELF-DIFFUSION, D , IN 1,2- DICHLOROETHANE.

coupling of the protons with chlorine nuclei⁷, intramolecular dipolar interactions modulated by rotamer exchange⁷² as well as rotational reorientation and the intermolecular dipolar interactions. There is no evidence for a significant contribution from spin-rotation interaction. Scalar coupling of the protons with chlorine nuclei might act as a relaxation mechanism for the protons because of the rapid quadrupolar relaxation of Cl^{35} and Cl^{37} nuclei. The expressions for T_1 and T_2 due to scalar coupling ($A \underline{I} \cdot \underline{S}$) of spin \underline{I} with a quadrupolar nucleus \underline{S} are given by⁷

$$\frac{1}{T_1} = \frac{2A^2 S(S+1)}{3} \left\{ \frac{\tau_2}{1 + (\omega_I - \omega_S)^2 \tau_2^2} \right\}, \quad (\text{VI.1})$$

$$\frac{1}{T_2} = \frac{A^2 S(S+1)}{3} \left\{ \frac{\tau_2}{1 + (\omega_I - \omega_S)^2 \tau_2^2} + \tau_1 \right\}, \quad (\text{VI.2})$$

where τ_1 and τ_2 are the spin-lattice and spin-spin relaxation times for \underline{S} and ω_I and ω_S are the Larmor precession frequencies of spins \underline{I} and \underline{S} respectively. In the present case $(\omega_I - \omega_S) \approx 60 \times 10^6$ and the quadrupolar relaxation times are usually of the order of a microsecond or longer. For $A (=2\pi J)$ where J is a few Hz in magnitude, it can be seen that the contribution of this interaction to T_1^{-1} is negligible. It contributes only to T_2^{-1} and can, sometimes, be observed as a broadening of the resonance of spin \underline{I} . For the discussion of T_1 results this interaction need not, therefore, be considered.

From the observed relaxation rates the intermolecular contribution can be separated by using Torrey's formula (see Eq. (II.38)). The density and viscosity data for this molecule are available in literature⁷⁰. Using the observed values of D along with viscosity data gives a hard-sphere radius ' a ' = 1.39 ± 0.05 Å for this molecule. The estimated intermolecular contribution is plotted in Fig. 29. It can be seen that the temperature variation of this interaction accounts for most of the temperature dependence of the observed relaxation rate.

Among the intramolecular dipolar interactions the interaction between the protons in each of the CH_2Cl groups are the most significant. (The interaction between protons on different group are comparatively weaker due to the larger internuclear separation). The molecular motion which modulates this dipolar interaction is likely to be rather complicated since, as is well known, the CH_2Cl groups undergo rotamer exchange by rotation about the C-C bond. The motion is, therefore, a hindered rotation superimposed on the molecular rotational diffusion. Hubbard⁷³ has considered the problem of hindered rotation of a CH_3 group superposed on the anisotropic rotational motion of the molecule containing the group and calculated the relaxation rate due to the dipolar interactions between the three protons. In the present case we are concerned with a single internuclear vector undergoing hindered rotation about the C-C axis. The correlation functions of angular orientation would include the correlation functions of the rotation of the

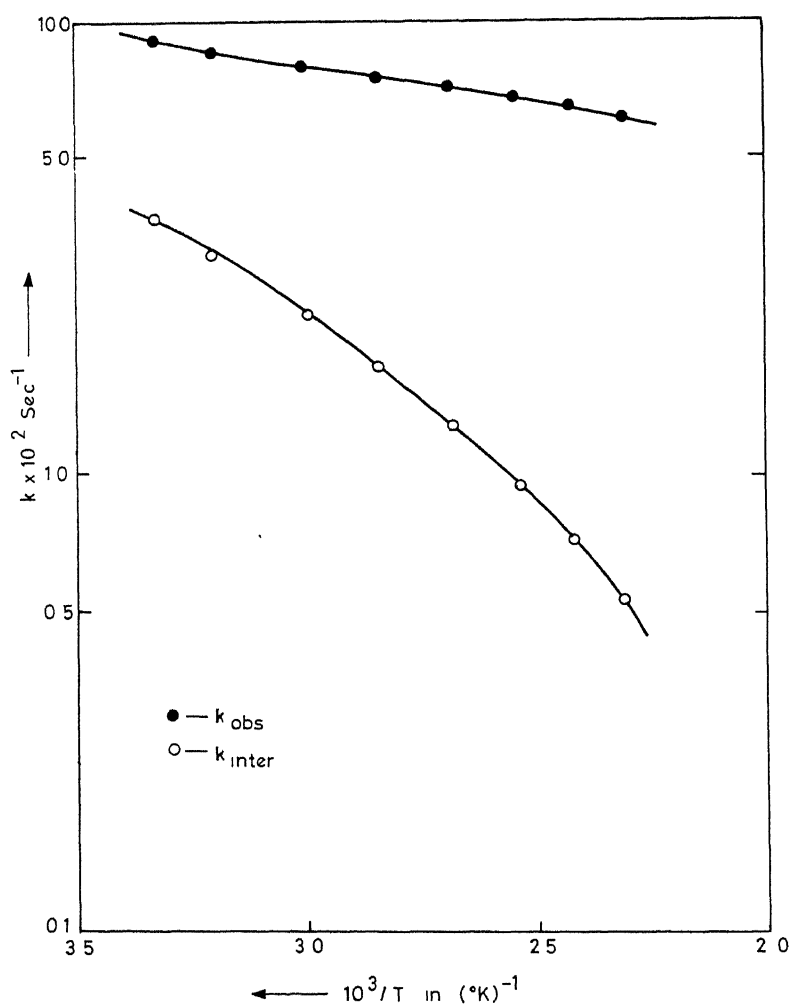


FIG. 29: PLOTS OF THE VARIOUS RELAXATION RATES IN 1,2- DICHLOROETHANE

internuclear vector in a molecule-fixed frame and also those of the orientation of the molecule-fixed frame with respect to a laboratory-fixed frame. Such correlation functions can be calculated for various models for hindered rotation. Using one in which the CH_2Cl group can assume three equally spaced angular orientations about its axis of rotation and the system jumps from one orientation to another with a probability $(\tau_R)^{-1}$ per unit time the spectral density is calculated to be⁷³

$$J(0) = \frac{2}{5} \frac{\gamma^4 \hbar^2}{r^6} \frac{1}{6D_x} \left[\frac{5D_x + D_z + 3(8\tau_R)^{-1}}{2(D_x + 2D_z) + 3(2\tau_R)^{-1}} \right], \quad (\text{VI.3})$$

where $D_x (=D_y)$ and D_z refer to the rotational diffusion constants along the x (in the plane of the triangle containing the two protons and chlorine nuclei) and z axis (C-C axis). τ_R gives the correlation time for rotamer exchange.

Whatever be the nature of motion the relaxation rate from intramolecular interactions can be written as

$$(\tau_1)_{\text{intra}}^{-1} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_{\text{eff}}, \quad (\text{VI.4})$$

where τ_{eff} is an 'effective' correlation time. Hubbard's calculation gives (from Eq. (VI.3))

$$\tau_{\text{eff}} = \frac{1}{6D_x} \left[\frac{5D_x + D_z + 3(8\tau_R)^{-1}}{2(D_x + 2D_z) + 3(2\tau_R)^{-1}} \right], \quad (\text{VI.5})$$

The correlation time for rotamer exchange can be calculated using the relation⁷²

$$(\tau_R)^{-1} = \frac{kT}{2\pi\hbar} \exp\left(-\frac{E_a}{kT}\right), \quad (\text{VI.6})$$

where E_a is the energy barrier for rotation. The values of E_a are known to be 5.3 and 5.1 kcal/mole respectively for the trans and gauche rotamer positions. In the temperature range of interest $(\tau_R)^{-1}$ varies from $3.4 \times 10^9 \text{ sec}^{-1}$ at 300°K to about $48.0 \times 10^9 \text{ sec}^{-1}$ at 430°K . The observed values of τ_{eff} are about 10^{-12} sec and hence rotamer exchange should give no significant contribution to relaxation. In the absence of rotamer exchange

$$(\tau_1)^{-1}_{\text{intra}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_r, \quad (\text{VI.7})$$

where τ_r is the correlation time for reorientational motion given by

$$\tau_r = \frac{1}{6D_x} \left[\frac{5D_x + D_z}{2(D_x + 2D_z)} \right], \quad (\text{VI.8})$$

if the motion is diffusional. From the experimental results on intramolecular contribution τ_r is calculated over the entire temperature range and is plotted in Fig. 30.

VI.C Discussion

It can be seen from Fig. 30 that τ_r varies very slowly with temperature. This behaviour indicates that the molecular motion in this case may not be diffusional (which usually results in an Arrhenius type of variation with temperature). Steele⁴¹ has obtained an upper limit on the value of τ_1 the correlation time for inertial type of reorientation of a

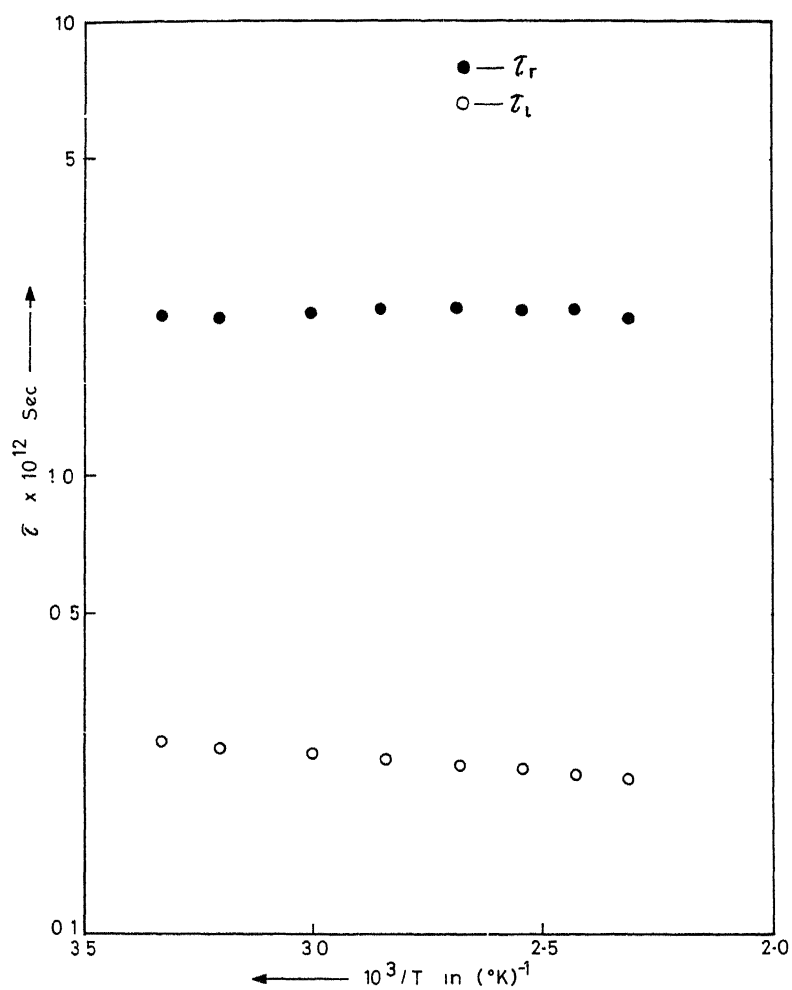


FIG. 30: TEMPERATURE DEPENDENCE OF τ_r AND τ_l IN 1,2-DICHLOROETHANE.

spherical top according to which

$$\tau_i \leq \frac{1}{2} \left(\frac{\pi I}{3k} \right)^{1/2} T^{-1/2} \quad (\text{VI.9})$$

For the case of dichloroethane I^{-1} has been replaced by $\frac{1}{3}(I_x^{-1} + I_y^{-1} + I_z^{-1})$ where I_x , I_y and I_z are the principal moments of inertia. From known values of I , τ_i has been calculated at various temperatures. These values are also shown in Fig. 30. These inertial correlation times are lower than the observed τ_r 's by almost a factor of 10. However, the trend in the temperature dependence of τ_i is similar to the experimental values.

Miller and Gordon⁷² have studied proton relaxation in a number of chloroethanes by determining T_1 and T_2 as a function of concentration in CS_2 at room temperature. They also find that the inertial effects probably determine the rotational motion in these molecules. The temperature variation of the rotational correlation time observed in the present work also points to the same conclusion. It may, however, be necessary to study other chloroethanes as a function of temperature and also compare the results with a theory which is rigorously applicable to them before concluding definitely on the inertial effects in their reorientational motion.

Chapter VII

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

In this chapter some of the significant results of this work are summarized and discussed.

The experiments consisted in the measurement of relaxation times as a function of temperature. The analysis of these results involve sorting out the various mechanisms that might contribute to relaxation in the system and then separating the contribution from each mechanism. In all the cases considered the intermolecular interactions have been estimated on the basis of a theory of translational diffusion given by Torrey²⁷ by using values of the coefficient of self-diffusion measured in situ using the spin-echo apparatus. This theory also involves a hard-sphere radius 'a' for the molecules. This radius is not related in any simple way to the molecular dimensions and may be considered as the radius of that equivalent sphere of which if the molecules of the liquid were composed the various macroscopic properties of the liquid would be reproduced. In the present work 'a' is estimated by using the reciprocal relationships between D and the coefficient of viscosity ' η ' on the basis of Stokes-Einstein formula. Although it does not seem possible to ensure that this is an accurate method the results indicate that in the absence of a direct method for determining this contribution this procedure is both useful and satisfactory.

Another important aspect considered in the analysis is that in molecules containing groups of spins which experience intramolecular dipolar interactions of different strengths the relaxation decays may contain multiple exponentials. Further, the relaxation rates are not linear superpositions of contributions from the different mechanisms but are complicated functions involving them, because of cross relaxation effects. This improves the accuracy of the determination of the relaxation parameters.

In thiophene and furan spin-rotation interaction contributes significantly to relaxation in addition to dipolar interactions as indicated by the maxima in T_1 vs $10^3/T$ curves. An analysis of the intramolecular interactions by the theory of anisotropic rotational diffusion¹⁵ led to the determination of the rotational diffusion constants ($D_{i=x,y,z}$) and angular velocity correlation times, τ_J , as functions of temperature. In performing the analysis τ_J is assumed to be isotropic to simplify the expressions involved. Although there is no a priori justification for this assumption the results indicate that it is satisfactory. The rotational diffusion constant perpendicular to the plane of the molecule, D_{\perp} , shows an Arrhenius type of temperature dependence in thiophene but not in furan, which is rather intriguing. It appears that in both molecules the reorientation departs from a diffusional character at high temperatures. The spin-rotation interaction constants have been estimated for both ^{the} cases. The substantial amount of

information gathered regarding the intricacies of the molecular motion in these systems is indicative of the usefulness of the spin-relaxation method for this type of study. Furthermore, this method is convenient for determining τ_J and estimating spin-rotation interaction constants of the order of a few kHz.

The rotational correlation times, τ_r , determined for 2- and 3-bromothiophenes show striking contrast in their dependence on temperature. In the temperature range 300°K to 450°K τ_r in 2-bromothiophene shows an Arrhenius type of dependence while it remains essentially constant in 3-bromothiophene. A slow variation of τ_r with temperature can be expected if inertial effects dominate molecular reorientation⁴¹. It is, however, not clear how the motion could be so widely different in character for two very similar molecules.

The temperature dependence of rotational correlation times in 1,2-dichloroethane show that inertial effects seem to govern the reorientation in agreement with the conclusion reached by Miller and Gordon⁷². A comprehensive study in several similar molecules may provide somewhat conclusive evidence for the same.

The spin relaxation method for the study of molecular motion has the limitation that it does not probe the 'shape' of the correlation functions but depends on the areas enclosed by such functions (correlation times). If the results obtained on the features of molecular reorientation in the liquids studied here

are an indication, it seems that this method is, nevertheless, capable of providing information of considerable value and significance in gaining insight into the liquid state.

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APPENDIX I

TEMPERATURE DEPENDENCE OF THE COEFFICIENT
OF SELF-DIFFUSION IN LIQUIDS

(Preprint of a paper by Anup Kitchlew and B.D. Nageswara Rao,
to be published in Mol. Phys. 21 (1971).)

TEMPERATURE DEPENDENCE OF THE COEFFICIENT OF SELF-DIFFUSION
IN LIQUIDS

The variation of the coefficient of self-diffusion, D , with temperature is of some interest in the study of the liquid state^{1,2}. In the present note measurements of D versus T are reported for ten different organic liquids in the temperature range 300°K to 380°K . The measurements were made using a spin-echo spectrometer operating at 9.78 MHz by using a $\frac{1}{2}\pi - \pi$ sequence in the presence of a uniform field gradient³. The details of the method and apparatus appear elsewhere⁴. The error in the D values is about ± 5 per cent. The experimental results are shown in figures A1 and A2.

The temperature and pressure dependence of D have been studied for several liquids by the N.M.R. method^{1-3,5-7}. Of the liquids chosen in the present work, to our knowledge, data exists only for benzene^{7,8}. Our value of D for benzene at room temperature agrees well with that obtained by the N.M.R. method and by the radioactive tracer method⁸. The temperature variation reported here is, however, larger than that obtained by the latter technique in the range 15°C to 45°C .

The Stokes-Einstein equation and also a hard-sphere model for liquids⁹ predict a simple relation between D and the coefficient of viscosity, η , viz. that $D\eta/T$ is essentially constant. The constancy of $D\eta/T$ was verified for the case of water^{1,2}. For all the liquids studied values of η in the

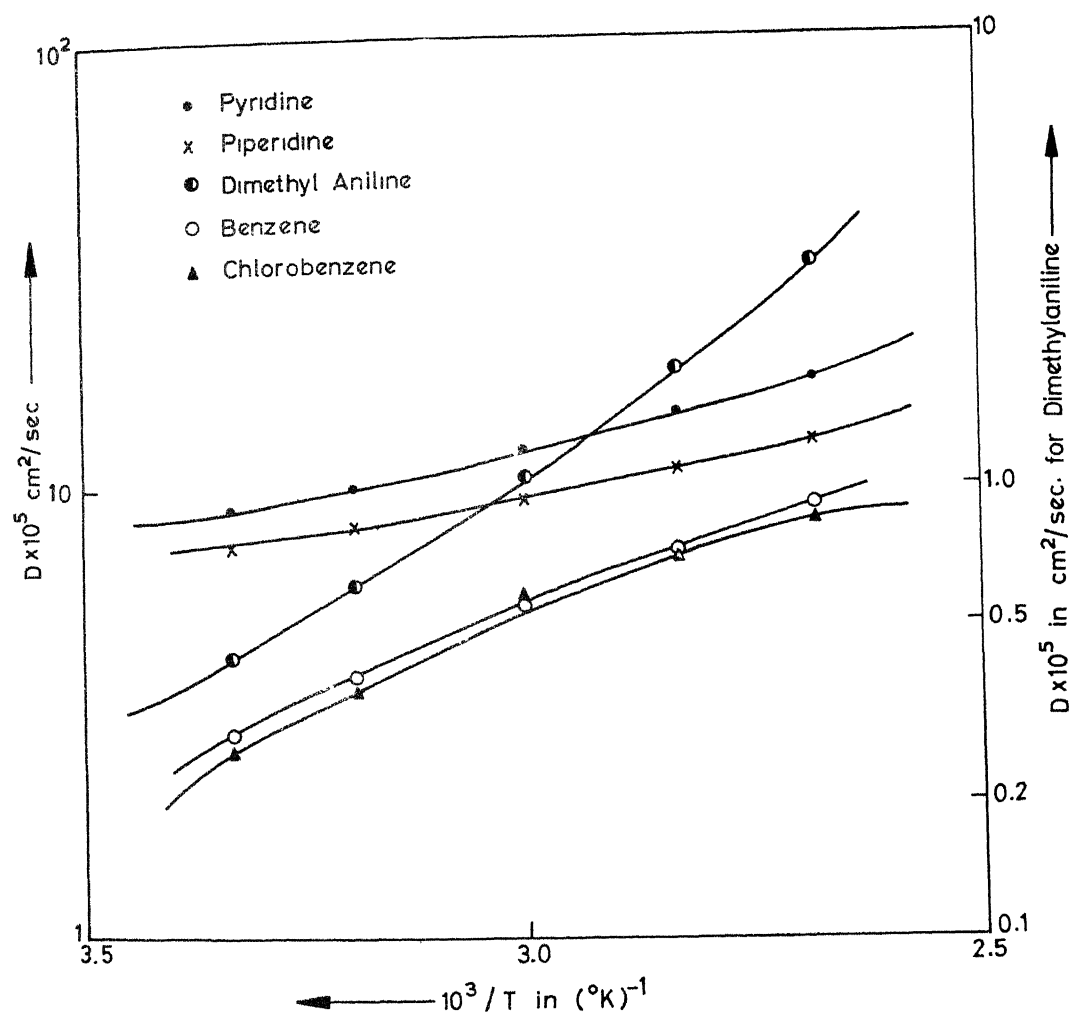


FIG. A1: VARIATION OF COEFFICIENT OF SELF-DIFFUSION, D , WITH TEMPERATURE FOR PYRIDINE, PIPERIDINE, DIMETHYLANILINE, BENZENE AND CHLOROBENZENE.

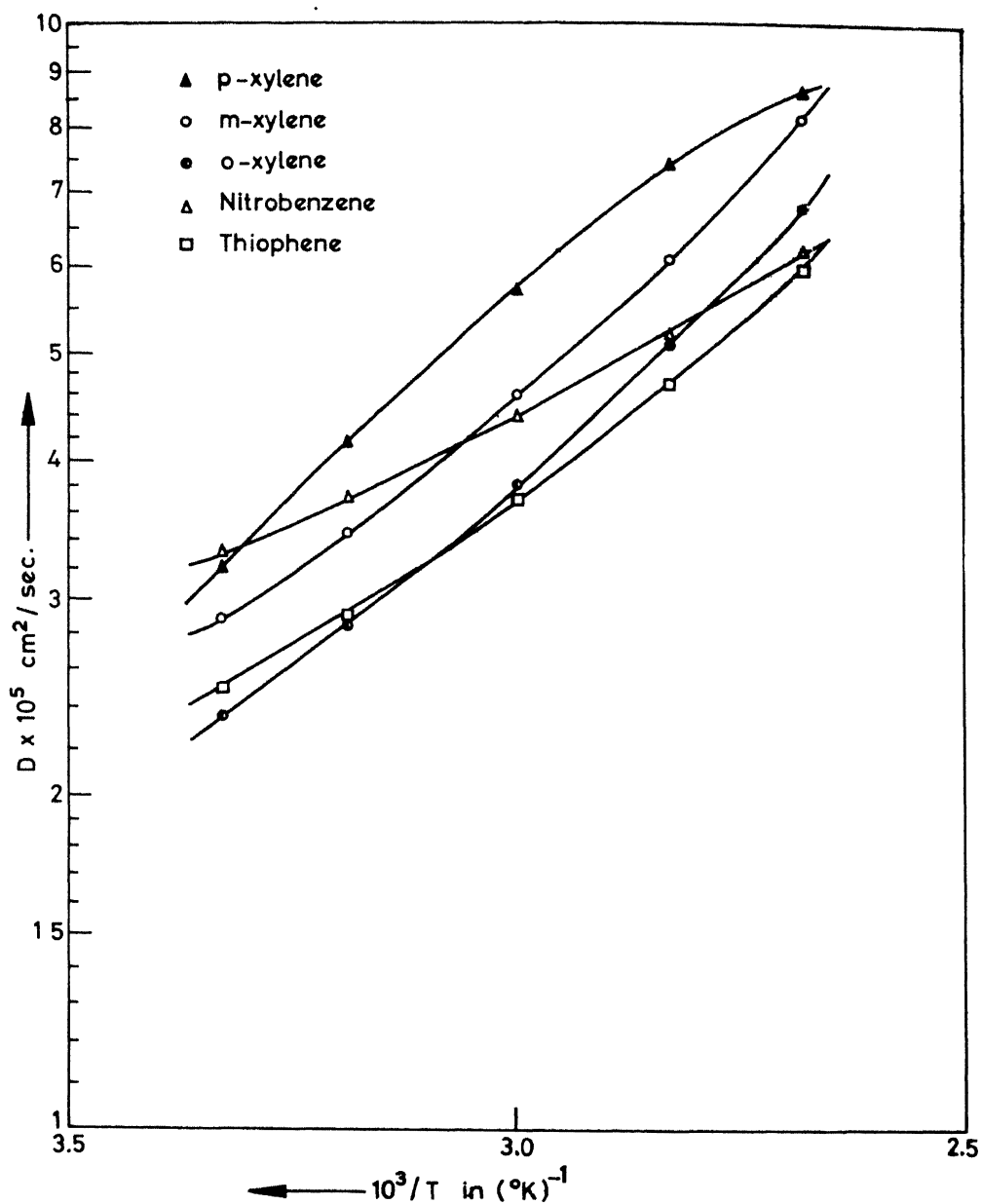


FIG. A2: VARIATION OF COEFFICIENT OF SELF-DIFFUSION, D , WITH TEMPERATURE FOR o-, m-, p-XYLENE, NITROBENZENE AND THIOPHENE.

temperature range of interest are available in the literature¹⁰. The quantity $D\eta/T$ at various temperatures was calculated using interpolated values of D and η . These are given in the table. For all but the last two liquids this quantity remains fairly constant. The activation energy for translational diffusion, $E_D \equiv -R \left[\partial \ln D / \partial (1/T) \right]$, calculated using figures A1 and A2, is also given in the table. In cases where $\ln D$ versus $1/T$ plots are not straight lines E_D is an average value.

If the average value of $D\eta/T$ is equated to $k/6\pi a$ (k is the Boltzmann constant) the hard-sphere radius ' a ' compatible with the Stokes-Einstein relation may be obtained. These radii for the first eight liquids are given in the table. For the three xylenes, benzene and chlorobenzene, the ' a ' values are nearly the same. In all cases ' a ' is smaller than the molecular dimensions and for pyridine and piperidine it is much smaller. If we use the expression given by Longuet-Higgins and Pople⁹ $D\eta/T = 3kc/10\pi a'$ where c is the fractional volume occupied by the molecules in the liquid and a' is the hard-sphere radius related to ' a ' used above, through $a' = (9c/5)(a)$. The value of c is not known in general, but even for $c \approx 1$, a' is still smaller than the molecular dimensions in most cases. While the variation of D and η seems to follow the temperature dependence predicted by the Stokes-Einstein equation and the hard-sphere model in most cases, the apparent hard-sphere radii seem not to have physical significance in either theory.

TABLE

.No.	Liquid	$D\eta/T \times 10^{10}$					a ° (Å)	E_D kcal/mol
		27°C	40°C	60°C	80°C	100°C		
1.	Benzene	5.47	5.95	6.45	6.32	6.22	1.20	3.5
2.	Chlorobenzene	6.40	7.15	8.26	8.32	8.10	0.96	3.7
3.	Pyridine	25.8	23.0	21.0	20.1	19.1	0.34	2.1
4.	Piperidine	32.1	25.6	22.3	22.0	23.0	0.29	1.6
5.	Thiophene	4.98	4.12	4.66	4.66	4.83	1.58	2.7
6.	p- Xylene	6.35	5.76	7.01	7.13	6.69	1.08	3.3
7.	o- Xylene	5.80	5.74	5.70	5.92	6.34	1.24	3.2
8.	m- Xylene	5.40	5.40	5.52	5.88	6.38	1.28	3.2
9.	Nitrobenzene	19.4	17.0	14.7	12.6	11.6	-	1.9
0.	Dimethylaniline	1.75	2.02	2.52	3.30	4.43	-	6.3

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APPENDIX II

ADDITIONAL DETAILS OF THE SPIN-ECHO APPARATUS

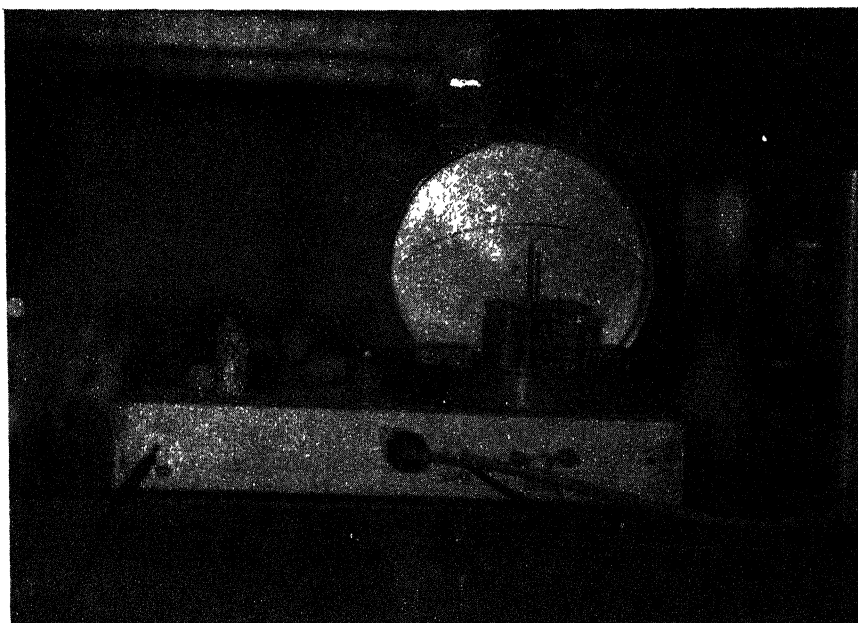


FIG. A3: LAYOUT OF THE OSCILLATOR

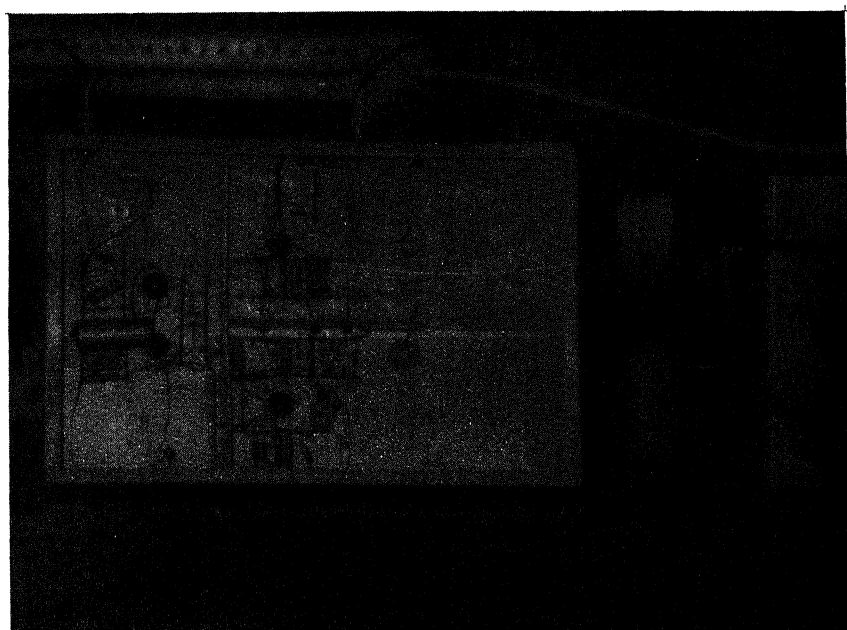


FIG. A4: LAYOUT OF THE GATE

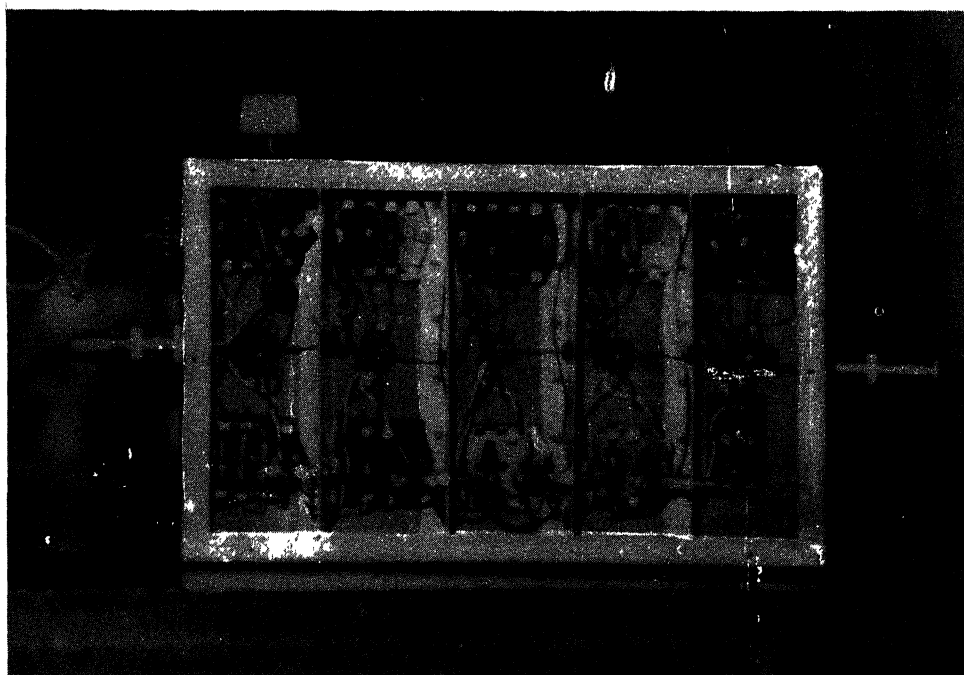


FIG. 45: LAYOUT OF THE RECEIVER

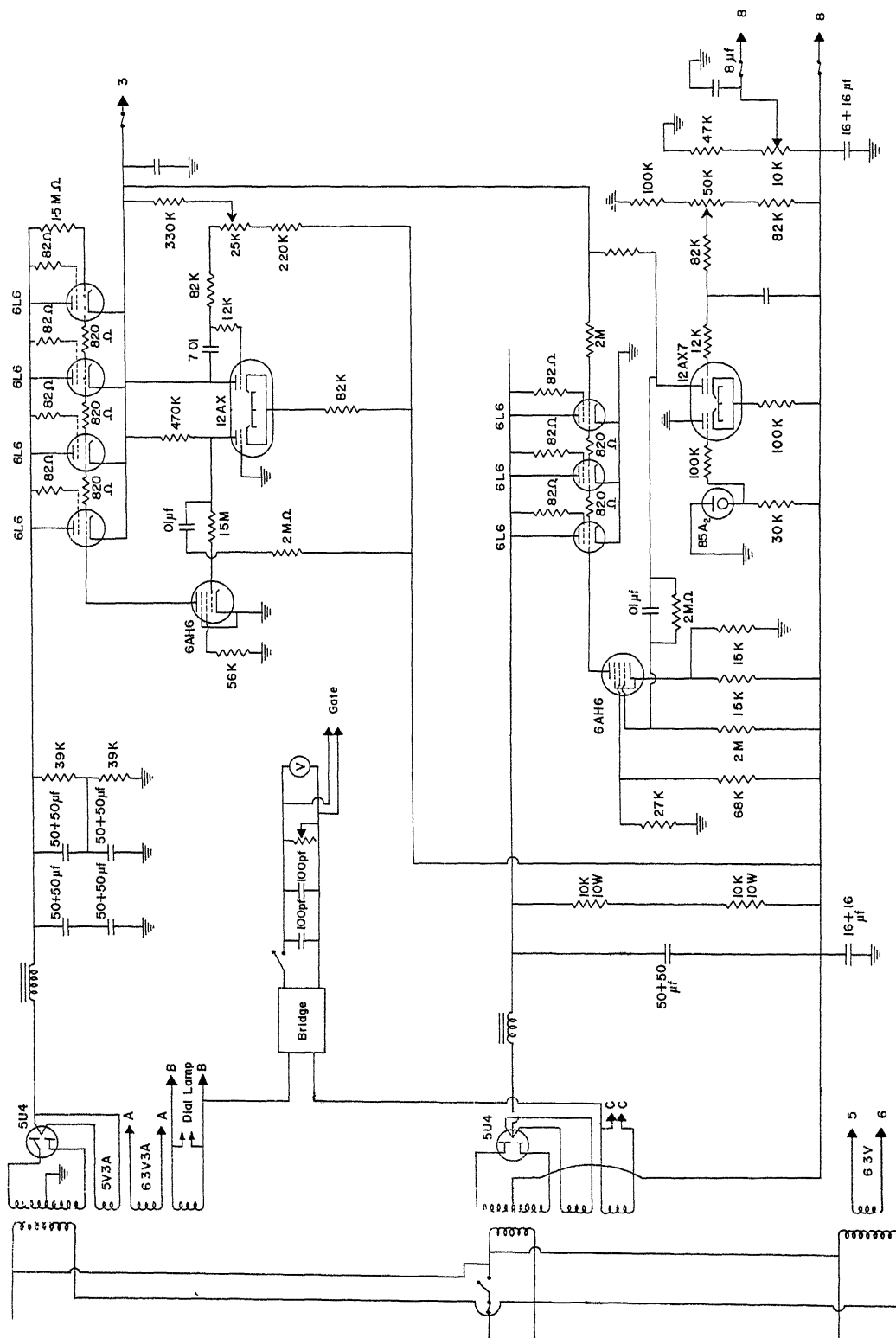


FIG.A6: POWER SUPPLY FOR THE GATED OSCILLATOR AND PULSE PROGRAMMER
(excluding the Tektronix units)

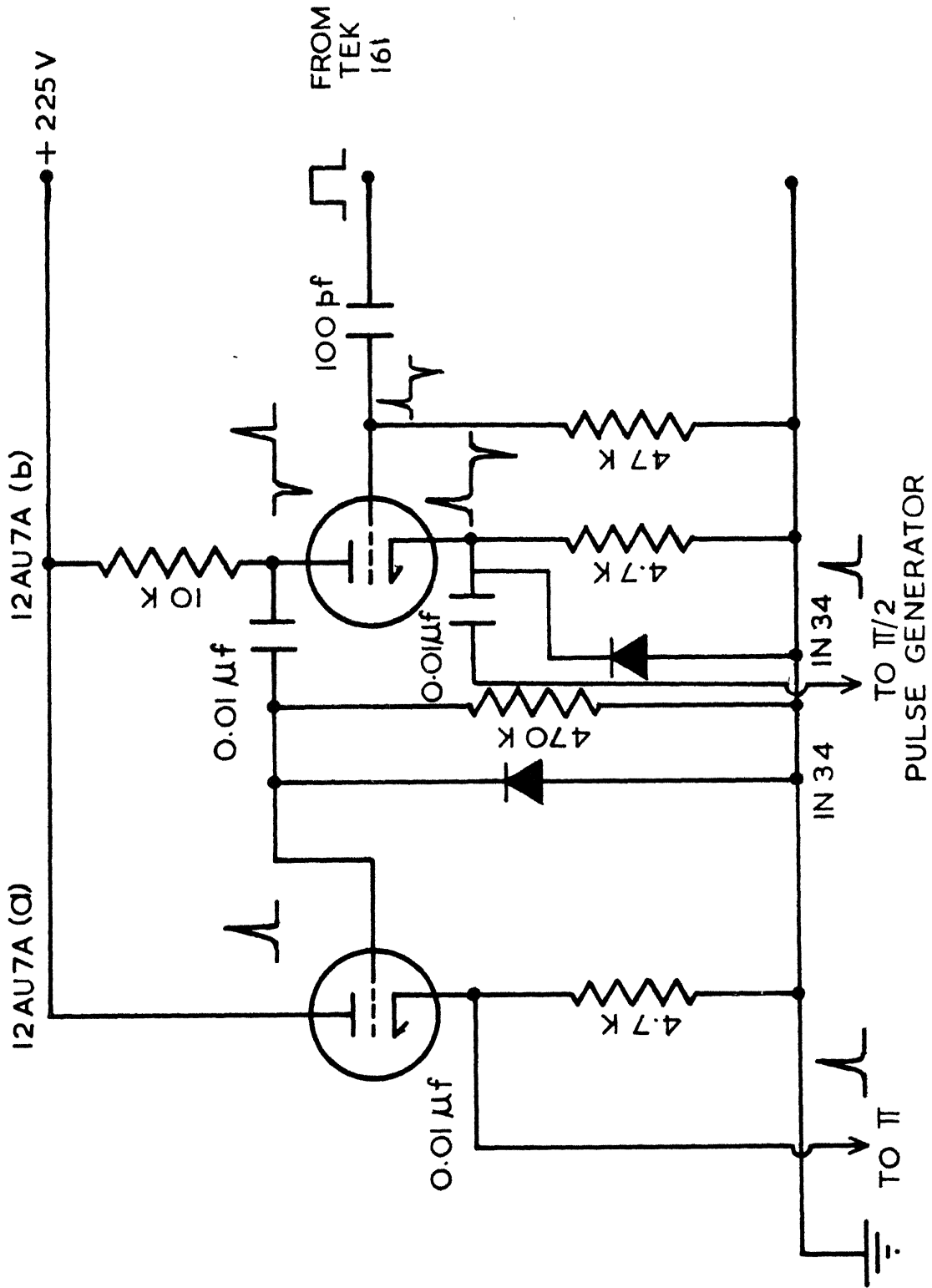


FIG. A8: DIFFERENTIATOR AND INVERTER

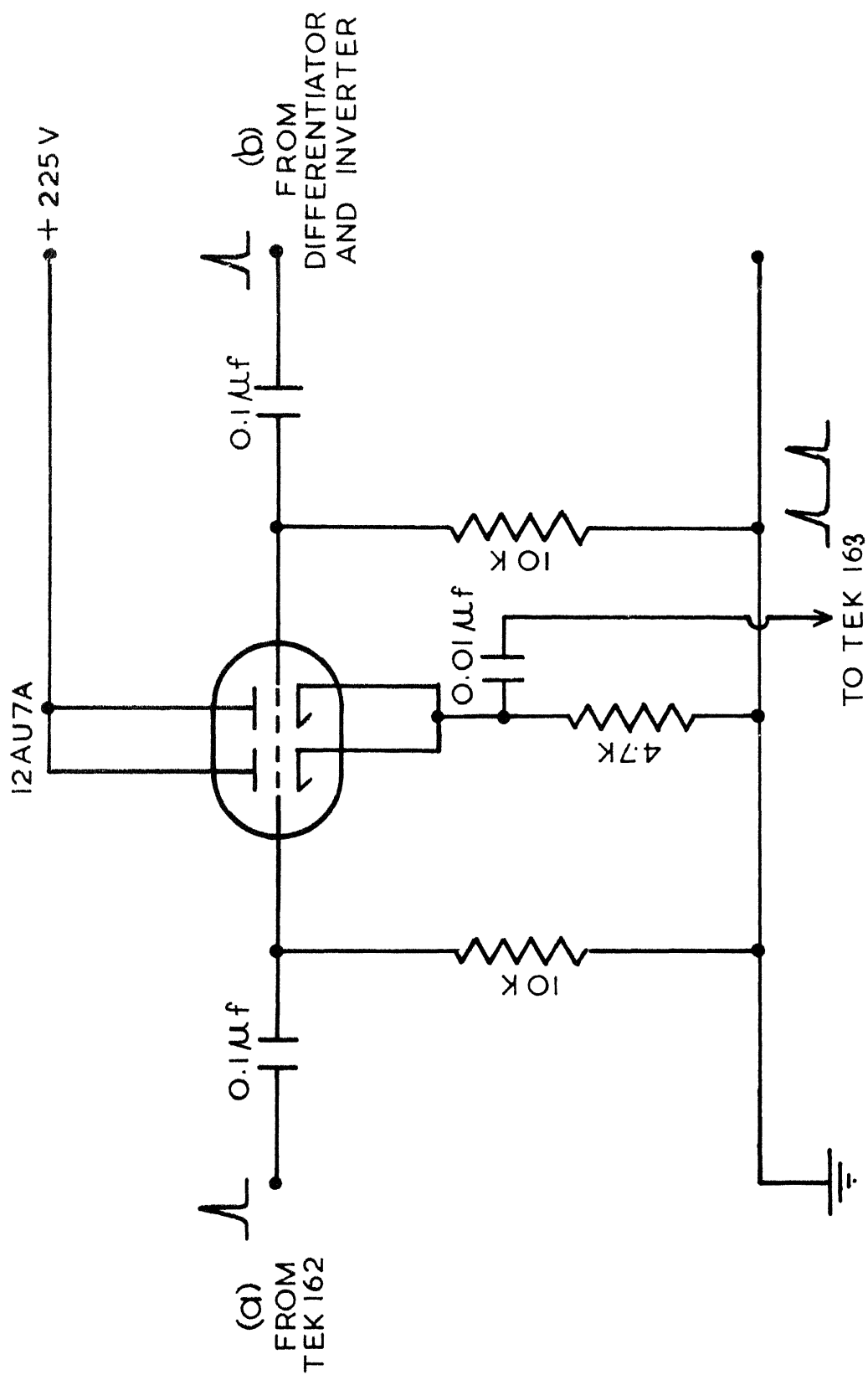


FIG. A9: TRIGGER MIXER

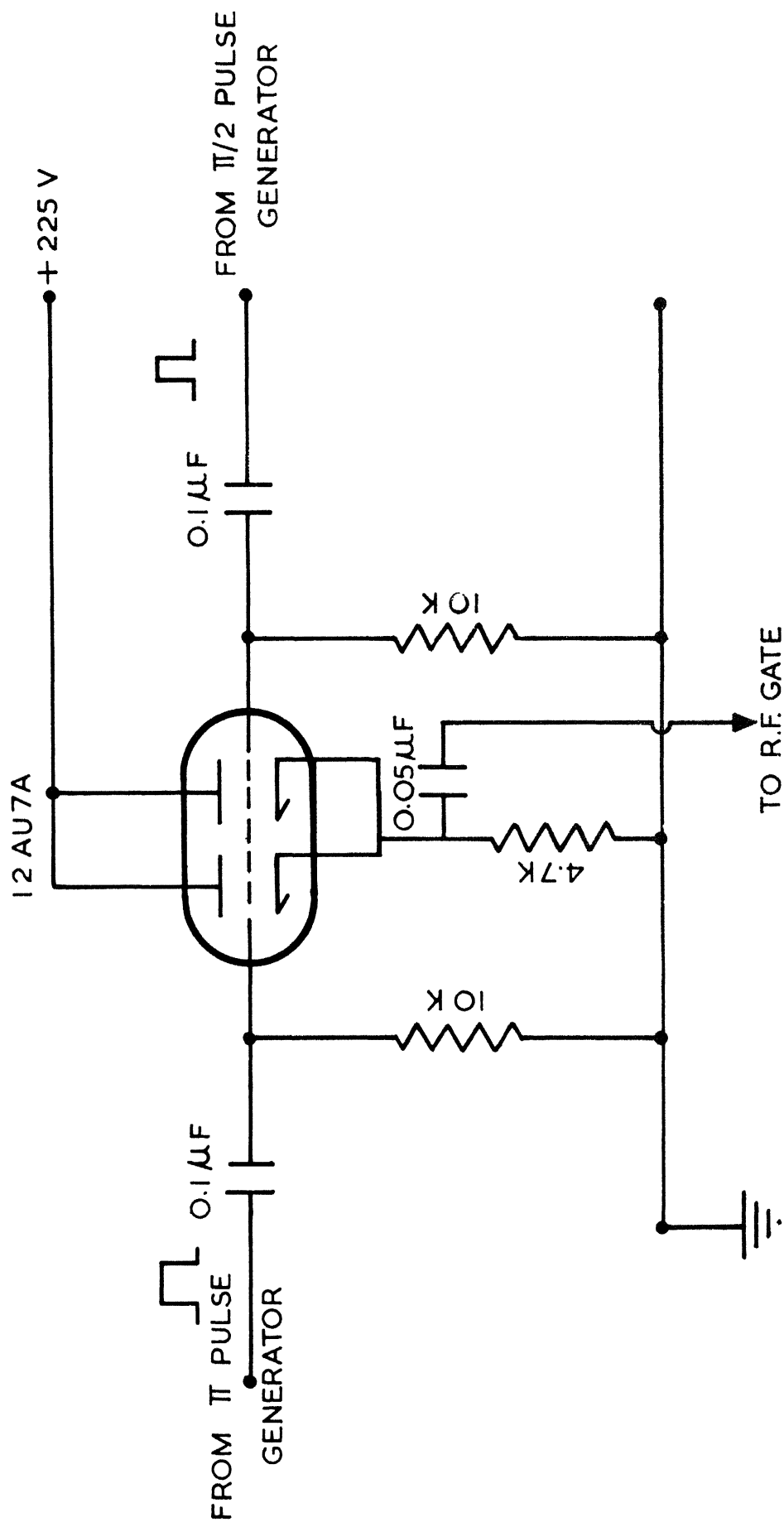


FIG. A10: PULSE MIXER

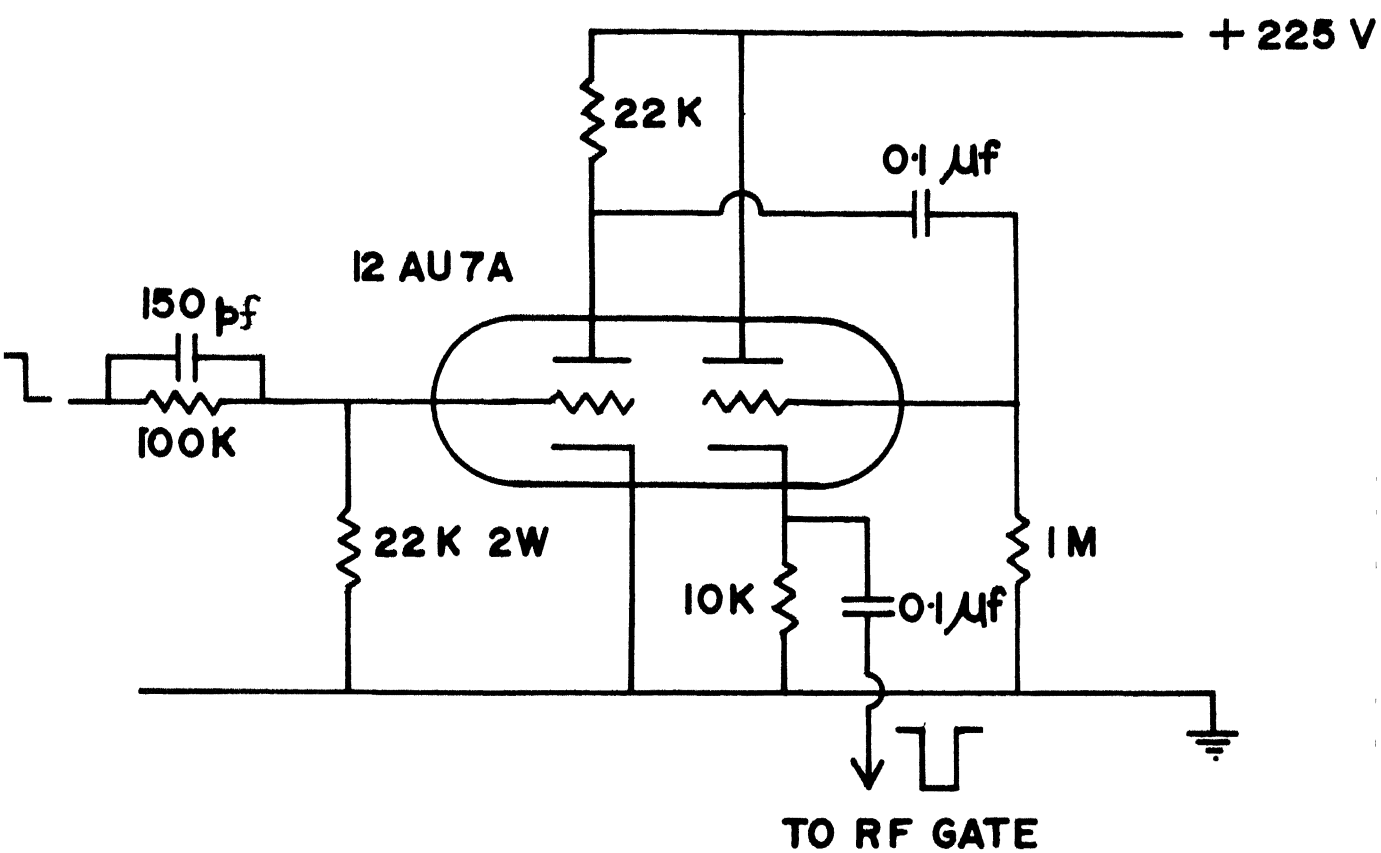


FIG.A11: PULSE INVERTER

APPENDIX III

MEASUREMENT OF T_2 BY CARR-PURCELL METHOD

MEASUREMENT OF T_2 BY CARR-PURCELL METHOD

A standard way of measuring T_2 would be to disturb the equilibrium magnetization by a $\pi/2$ -pulse which tips the entire magnetization into the xy-plane. A π -pulse applied at an interval τ after the $\pi/2$ pulse gives an echo (at a time 2τ) the height of which would be a measure of the magnetization in the xy-plane at that time. Varying τ would indicate the rate of decay of this magnetization.

It has already been explained in Sec. III.D that since the spins are located in an inhomogeneous field the relaxation decay would be superimposed by an additional dephasing of the isochromats because of diffusion. The decay following a $\pi/2$ - π sequence in the presence of a constant field gradient, G , is of the form^{1,2} (see Eq. (III.8))

$$M(t) = M(0) \exp\left(-\frac{t}{T_2} - \frac{D\gamma^2 G^2 t^3}{12}\right). \quad (1)$$

Carr and Purcell¹ have suggested a method of obtaining an echo envelope which reveals the natural decay due to relaxation even in the presence of diffusion. In contrast with the method described earlier, in this method the entire decay is obtained in a one-shot experiment. A series of π -pulses at interval 2τ from each other, are applied at a time τ after an initial $\pi/2$ -pulse. At the times $2\tau, 4\tau, \dots$ etc., there will be echos

because the effect of each π -pulse would be to reverse the direction of the dephasing isochromats. Carr and Purcell have shown that the effect of interpolating a large number (n) of π -pulses in an interval of duration t is to reduce the mean square phase dispersion by a factor $1/n^2$. Thus the decay is given by an expression of the type^{1,2}

$$M_{CP}(t) = M(0) \exp \left(-\frac{t}{T_2} - \frac{\gamma^2 G^2 D t^3}{12 n^2} \right), \quad (2)$$

and at any instant $t = 2n\tau$

$$M_{CP}(t) = M(0) \exp \left(-\frac{t}{T_2} - \frac{\gamma^2 G^2 \tau^2 t}{3} \right). \quad (3)$$

A plot of $M_{CP}(t)$ versus t would, therefore, be an exponential in spite of diffusion. For small τ 's the time constant of the decay is essentially T_2 .

Experimental Arrangement for Obtaining a Carr-Purcell Sequence:

An experimental arrangement for obtaining a Carr-Purcell sequence, due to Meiboom³ is shown in Fig. A.12. A switch S normally closed is pressed to give a voltage step which triggers a Tek 162 waveform generator which in turn gives

- (a) a single pulse at the moment the voltage step is applied,
- (b) a recurrent sawtooth as long as the switch is kept pressed.

The single pulse obtained when the switch is pressed is used to trigger the $\pi/2$ -pulse generator and the recurrent sawtooth triggers the π -pulse generator. The two kinds of pulses are mixed and used to gate the r.f. oscillator. The

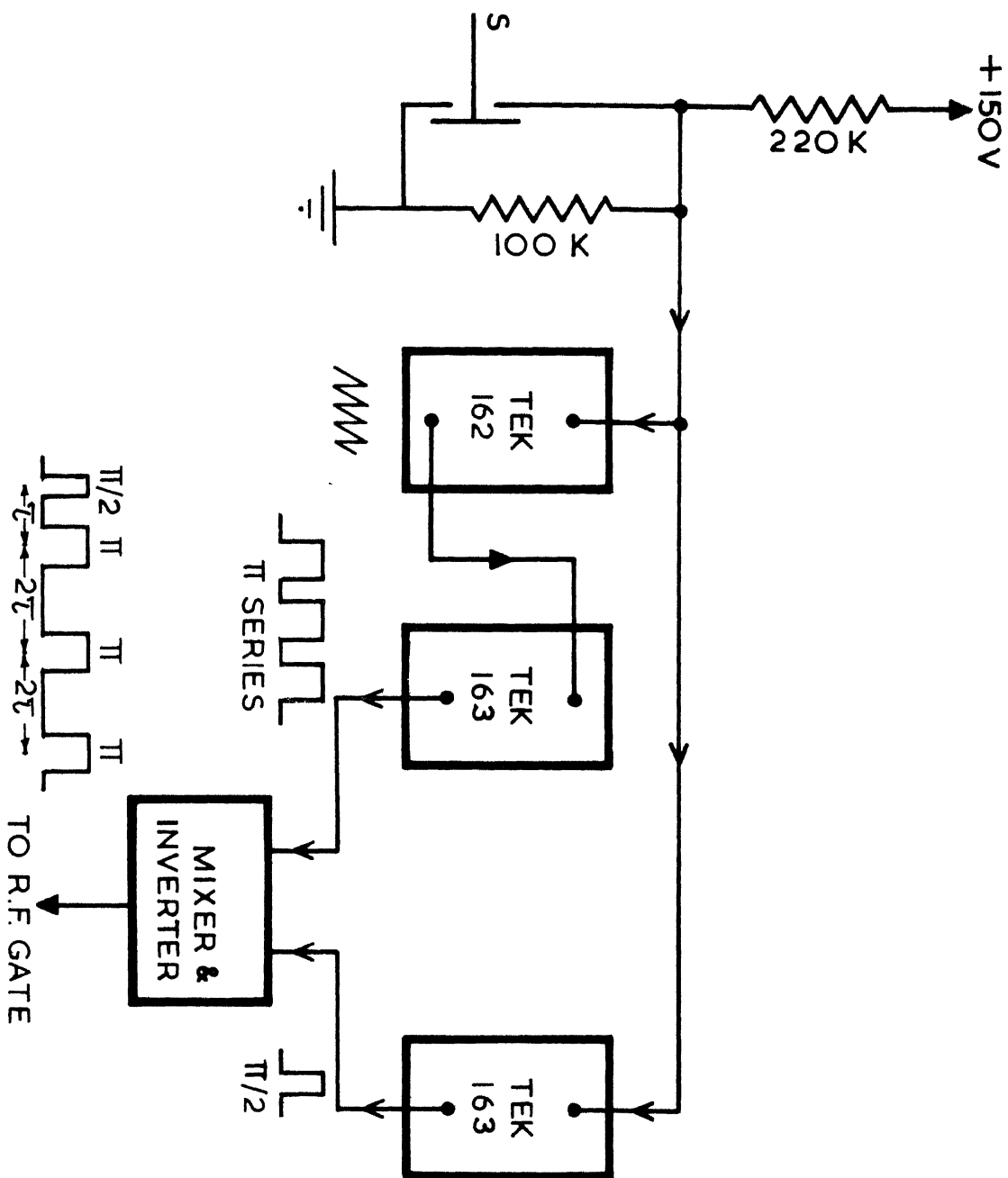


FIG. A12: EXPERIMENTAL ARRANGEMENT FOR OBTAINING A CARR-PURCELL SEQUENCE.

interval between the $\pi/2$ and the first π -pulse is adjusted to be half that between the subsequent π -pulses by triggering the π -pulse generator at the midpoint of the sawtooth. A typical Carr-Purcell decay for proton resonance in glycerine is shown in Fig. A.13.

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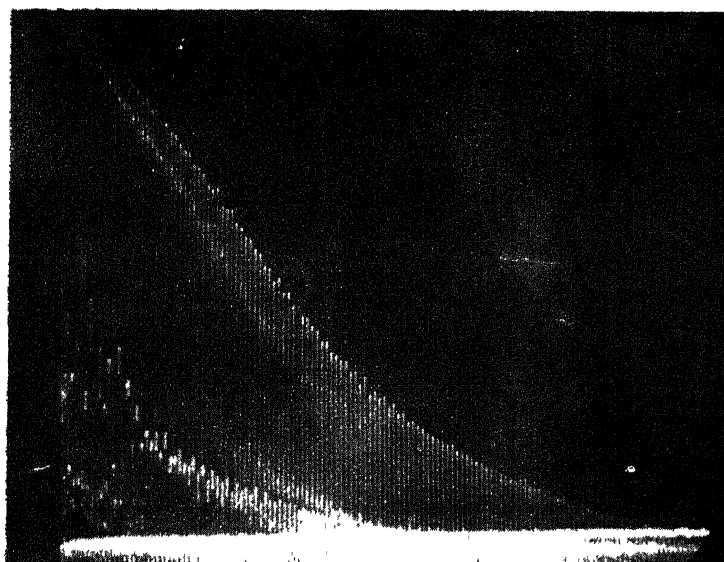


FIG. A13: CARR-PURCELL SPIN-ECHOS IN GLYCERINE
($\tau = 0.25$ m secs; $\tau_2 = 21.5 \pm 2.0$ m secs.)